INSTITUTE NOTES.

FEBRUARY 1940.

CANDIDATES FOR ADMISSION.

The following have applied for admission to the Institute or transfer to another grade of membership, and in accordance with the By-laws the proposals will not be considered until the lapse of at least one month subsequent to the issue of this *Journal*, during which any Fellow, Member or Associate Member may communicate by letter to the Secretary, for the confidential information of the Council, any particulars he may possess respecting the qualifications or suitability of any candidate.

The object of this information is to assist the Council in grading candidates according to the class of membership.

The names of the candidate's proposer and seconder are given in parentheses.

ALLCARD, Harry Ganly, Director (*H. G. Allcard & Co., Ltd.*), "Ravenswood," Wythanshawe Road, Northenden, Manchester. (*J. E. Haslam; A. McCulloch.*)

ANDERSON, William Archibald, Information Officer (*N.S. Wales Government Railways*), 19, York Street, Sydney, N.S.W. (*O. Colverd.*)

CARTER, Edward Howard, Transport Manager (*G. & T. Earle, Ltd.*), "Beaumaris," 44, Carr Lane, Willerby, E. Yorks. (*J. E. Haslam; H. S. Kernan.*)

FORSTER, Denis Williams, Chemist (*J. White & Sons, Ltd., Widnes*), "Woodlea," Brookside Avenue, Sankey, Nr. Warrington, Lancs. (*A. McCulloch; J. E. Haslam.*)

MOND, Albert Levy, Chemical Engineer, 14/18, High Holborn, London, E.C.1. (*V. Henny; E. N. Hague.*)

PARTRIDGE, William Arthur, Chemist (*Anglo-Iranian Oil Co.*), 10, Norman Court, Upper Sunbury Road, Hampton, Middx. (*A. E. Dunstan; F. B. Thole.*)

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PRESIDENTIAL ADDRESS.

THE DEVELOPMENT OF PETROLEUM REFINING.*

By Professor A. W. Nash, M.Sc.

The purpose of this address is to record briefly, and in historical sequence, those developments in petroleum refining which have been of the greatest importance, in so far as they have led to present-day practice, bearing in mind that time and space do not permit of a comprehensive review of all phases of the subject.

At one time the sole activity of the refiner was that of distillation, and so little has the principle changed that even to-day distillation is the major function of the art of refining.

Distillation processes have been used by the earliest experimentalists, and Pliny (A.D. 23–79) describes a method of obtaining rosin oil by the application of heat followed by a primitive method of condensation. The Alexandrians are reported as having prepared oil of turpentine by distilling pine resin, whilst improvements in condensation apparatus are attributed to the Arabians, who are said to have been responsible for the discovery and extraction of a number of essential oils, and of alcohols from wine, by distillation methods.

In the work of Zosimus (*circa* A.D. 400) are described and illustrated certain types of distillation utensils, based upon apparatus which he saw in use in the Temple of Serapis at Memphis, one of the chief alchemical laboratories of that time.

Although the art of distillation had been known for several centuries, it would appear that alcohol distillation was not practised on any large scale until the eleventh century, when the alcohol industry as then established became the pioneer of all the distillation processes. Subsequently distillation came into use not only in the petroleum industry, but also in many other industries.

Distillation.

The general principles involved in distillation are, like most principles in science, very simple in outline, but most complicated in detail.

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* Address delivered at a meeting of the Institute of Petroleum held in London on Friday, 26th January, 1940.

Petroleum is a very complex substance, and in its conversion into vapour and its subsequent condensation into liquid the known scientific principles underlying the separation of simple mixtures cannot be applied with any high degree of accuracy to a process which is undoubtedly nothing more than an art.

Nevertheless, the distillation of petroleum, and its fractionation into the products then marketed, were carried out quite successfully in the earlier days, although it is doubtful if many refiners appreciated the part played in such processes by the hypotheses of Dalton (1801) and of Avogadro (1811), or by the law of Raoult (1883).

The simplest distillation apparatus, so well known to the "moonshiner," consisted of three parts: the still, the condenser and the receiver. These three parts are just as much essentials in the more complicated designs of present-day plant, the only addition of major importance being that of the fractionating column.

In this latter respect we owe much to Wurtz, Linneman and le Bel, and to Henninger for their ideas on fractionation, whilst the credit for the development of reduced-pressure distillation is due to Dittmar and to Anschutz. To Liebig we owe the laboratory condenser, and the development of the reflux condenser is due to Kolbe and to Frankland.

The coal oil produced by James Young (1847) was found to be unsatisfactory when used as a lamp oil to replace whale oil, which was becoming increasingly scarce at that time, and this demand for an alternative source of supply led to a rapid development of petroleum refining for burning-oil purposes. This was followed by an increasing demand for lubricants much in excess of the supply of animal, vegetable, and fish oils for this purpose, with the consequent increase in the number of petroleum refineries.

The earliest stills used in the distillation of petroleum were replicas of those which were then used in the coal-oil industry. These were heavy cast-iron vessels, round in shape, with capacities ranging from 200 to 2000 gallons, the only instrument of control fitted being a thermometer.

Although horizontal cylindrical stills, of much larger capacity and made of thin wrought-iron plate, were introduced in 1860, it was not until 1885 that the continuous-shell-still method of distillation came into general use. At about the same time Leet pointed out the advantages of bubble-tower rectification as used in the alcohol industry and recommended its use in petroleum refining. Nevertheless it was not until thirty years later that his advice was accepted by the petroleum industry, after some ten years' experimentation with packed towers.

It is true that for some years Heckmann had been using, in Europe, a column based on this principle for the redistillation of benzene from shell stills, reflux being obtained by means of a partial condenser, but such a principle was not in general use for many years after.

In the year 1905, or thereabouts, a number of packed vertical towers, stone being at first used as the filling, followed by baffle-plates, were fitted with partial condensers and used in the United States by the Standard Oil group, but it was not until difficulty was experienced in dehydrating the heavy California crude oil in shell stills that pipe-stills were first tried out for this purpose in the petroleum industry, although they had been used in coal-tar distillation as far back as 1890. These pipe-stills soon came into general use largely due to the efforts of Trumble, Fuqua, and of Bell. By 1911 pipe-stills and dephlegmating towers were used almost throughout California, and gradually spread to other fields in the United States.

Their development outside of America hung fire for some years, but as a result of an attempt in 1920 to standardize specifications of petroleum products, particularly those of gasolines, kerosines, and certain lubricating oils, the problems of the plant designer were very much simplified. The industry is now in possession of fractionating equipment of such flexibility and accuracy as has resulted in a remarkable reduction in the cost of manufacture of refined products, thus enabling the consumer to purchase at a price, until recently, unprecedented in the history of petroleum.

In considering the development of pipe-stills, of particular interest was the Trumble plant first used in 1911. The original large tubes were subsequently reduced considerably in diameter when the importance of radiant heat was appreciated by engineers responsible for furnace design. Thus the present-day multi-pass tubular stills, with their accurately machined return bends, may be said to owe their origin to Trumble. The advantages of the baffle-plate air-cooled dephlegmator and the heat exchanger, the former reducing the amount of re-running necessary and the latter effecting a considerable saving in cooling water and fuel costs, soon became evident. Great improvements have since taken place in regard to condensers : from the old worm condenser, containing coils of comparatively large-diameter pipe submerged in water, we now have nests of small tubes with multi-pass arrangements, which make for efficient heat transfer, together with floating heads, which allow for expansion, thus eliminating leakages.

An indication of the advance made in the distillation process of petroleum refining is best measured by a comparison of heat transfer then and now. In the radiant heat section of modern pipe-stills,

35,000 B.Th.U. per square foot projected area per hour are possible when necessary, as compared with 4000 B.Th.U. maximum in the old shell stills.

The reduction in the quantity of oil being heated as the result of the introduction of pipe-stills necessitated much closer control of operating conditions, with the result that automatic devices for recording and controlling temperatures and liquid levels were introduced. These devices have now reached a high standard of precision, largely due to the practice of cracking, which was established about the year 1920, the four most important processes then in existence being those of Burton, Dubbs, Cross, and Greenstreet.

The last three processes made full use of the knowledge which had then been acquired regarding the value of pipe-stills, baffle-plate towers, and heat exchangers, to be followed by the use of the bubble-towers introduced as the result of experience in casing head gasoline extraction. Thus forty years after Leet's attempt to popularize the bubble-tower in petroleum refining, it became firmly established in 1925.

Although advances have been perhaps greater in the design of pipe-stills than in any other branch of petroleum distillation, nevertheless the most important improvements which have taken place are undoubtedly in connection with fractionating towers, probably due to the longer experience of the distillers of alcohol. The present-day multiple side-stream fractionating tower, really a combination of several fractionating towers in one unit embracing vapour heat exchangers in connection with side strippers, the closeness of fractionation of which depends so largely on adequate reflux ratio, has resulted in a marked increase in thermal efficiency and in the cleaner separation of fractions. Indeed, the gap between the end-point of one fraction and the initial boiling point of the next shows that the modern bubble-tower can give much closer separation than the standard Engler flask, a fact which would have been hard to realize in 1926, when these towers were first installed on a commercial scale.

Cracking.

As a result of the developments just referred to, the art of cracking benefited to an even greater extent, and to-day it may be said that distillation and cracking plants are so flexible as to be capable of handling practically every type of crude oil or distillate, from the heaviest oils to the lightest spirits, or even gases.

The cracking process has contributed more towards the conservation of crude oil than any development in the history of the petroleum industry, for to have produced all motor-fuel requirements from

straight-run gasoline would have necessitated the raising of enormous quantities of crude oil, with the subsequent production of other fractions, far in excess of requirements. This would have led to such waste as to have upset the economic efficiency of the petroleum industry of the world, because to-day nearly half of the gasoline consumed is produced by cracking.

The earlier experimental work on pyrolysis by Faraday (1830) and by Berthelot (1860) merits record, whilst Young (1865) and Dewar and Redwood (1889) were undoubtedly pioneers of the present highly efficient methods of cracking which are capable of converting the most unpromising crude oil and heavy and medium residues into gasolines of much higher grade, judged by the present-day standards, than most of those obtained by straight run distillation. In paying such tribute the names of Burton, Ramage, Greenstreet, Hall, Rittman, and MacAfee should also be mentioned.

Able to profit from the use of pipe-stills which had then become established in distillation practice, the designers of those original plants which have since acquired commercial success at first based their plans on empiricism and the technology of cracking acquired by experience. A study of the thermodynamics and chemistry of cracking has helped considerably in improving the design of these plants, and a better understanding of time and temperature relationship led to the knowledge of the advantage of separating the heating and reacting zones, which resulted in the rapid development of such processes as the Cross, Dubbs, Tube and Tank, Jenkins, and the Holmes-Manley.

The increasing demand for gasolines of higher anti-knocking qualities was a cause of the return to the so-called vapour-phase methods of cracking, such as the modified Gyro process, that of De Florez and the True Vapour-Phase process, but Midgley's discovery (1923) of the value of lead tetraethyl as an anti-knock dope resulted in a check to the further development of vapour-phase cracking, as such, for a short time.

With the higher cracking temperatures now in use, it is impossible to distinguish between liquid- and vapour-phase conditions, but if the present demand for high-octane fuels continues, it is probable that straight-run spirits will not have a ready sale in the future, unless they have been thermally treated previously. It is for this reason that the process, known as reforming, has advanced to such an important position in refining to-day, and the gases formed by this and vapour-phase cracking are now proving of extreme value as a source of raw material for chemical synthesis, a subject which will be discussed later.

Simultaneously with these developments experiments were being carried out to produce heavier oils in the lubricating range without destroying their lubricating properties as the result of decomposition, and so 1930 saw the introduction of the low-absolute-pressure cylindrical-still units of Schultz and of Steinschneider, which were later converted into continuous multiple still operations. The principle of these units has since been adopted in pipe-still and bubble-tower operations, although not necessarily confined to the production of lubricants only.

The next aim of the plant designer was to combine the distillation and cracking processes in one unit, which culminated in the first of the very large modern combination units being erected in 1932 for the Standard Oil Company of Indiana.

To-day combination units are running with a throughput as high as 1½ million gallons a day, which include as an integral part of their process, crude topping, primary cracking, vapour-phase cracking, fuel-oil flashing, reforming and vapour-phase refinement resulting in a very high rate of heat conservation and the maximum production of gasoline of comparatively high octane value.

In this latter connection the future possibilities of catalytic cracking should here be considered.

Whilst catalytic cracking was known in the earlier days of experimental pyrolysis, it has but recently been employed in commercial practice on a large scale, and units are now in operation with throughputs as high as 600,000 gallons daily.

Some of the chief claims of the Houdry method are liquid recoveries as high as 99 per cent., with a corresponding decrease in gas and coke production yielding gasoline of 80 C.F.R.M.M. octane numbers from any type of charging stock heavier than gasoline, suitable as base stock for aviation fuels.

Mention should here be made of a method of catalytic reforming known as cyclization, which, as its name implies, can convert hexane into benzene, heptane into toluene, etc., and is a much more valuable source of aromatics than the older method of gas pyrolysis so well known to us through the researches of the late Professor R. V. Wheeler.

Where products other than gasoline are of importance there are available the combination of high-vacuum pipe-still distillation, bubble-tower fractionation aided by flash jugs, efficient heat-exchanging devices, and modern instrument control of such a high degree of efficiency as to enable the refiner to produce a more uniform product at a much lower cost than previously from a wider range of raw materials. This has been reflected in the cheapness with which the

consumer can purchase his requirements despite the burden of taxation which the products of petroleum have had to bear in this country.

Refining.

It has been stated that the progress of chemical science throughout the ages can best be measured by the quantity of sulphuric acid used throughout the civilized world, and this statement applies no less to the petroleum industry.

One of the earliest uses to which petroleum was applied was that of illumination, and as a result of Scottish shale-oil practice, which originated with Young in 1847, sulphuric-acid treatment followed by caustic-soda washing became universal throughout the industry; in fact this process is still the most common method to-day for the removal of undesirable components from burning oil and other distillates, particularly cracked spirits.

It was not until 1884 that lubricating oils were first produced on a large scale as overhead products, an improvement ascribed to Samuel Downer, who was also responsible for the chilling of oils followed by the pressing of wax as carried out by earlier manufacturers on exactly the same principle as that employed at the present time.

Exactly when the adsorptive properties in filtration were first utilized by our industry cannot be traced, but the phenomenon of adsorption was reported by Scheele in 1773, and bone black had been used for filtering for centuries before the advent of Florida earth in the petroleum industry about the year 1898. By 1906, however, Florida earth was in common use by manufacturers of lubricating oils, and at the same time sweating was introduced for the manufacture of wax of varying degrees of hardness, an operation which was substantially the same then as at the present time.

Some few years after this there arose a demand for lubricants for petrol engines, a demand which has been growing ever since, and the contact method of filtration for the stabilization of acid-treated oils was investigated by Gray; a study which undoubtedly led to his method of vapour-phase treatment of cracked spirits.

In 1885 Frasch was responsible for a process of refining in which kerosine was distilled over black copper oxide, a discovery which was followed by several processes for the removal of merceptans by forming their metallic derivatives.

Cold settling was discovered quite by accident in 1890, and in 1894 the present low-cold-test and bright-stock development had become firmly established. This was followed in 1920 by centrifuging,

which opened up a new source of supply of bright stocks from crude oils other than of Pennsylvania origin. To-day, however, both crystalline and amorphous types of wax, and mixtures of both, are successfully extracted by the solvent dewaxing process, using either single-component solvents or two-component solvents, and it is probable that most dewaxing installations will be of the solvent type in the near future.

Of the so-called physical methods of refining the use of bauxite was amongst the earliest, and this method was originated by the Burmah Oil Company at their Syriam Refinery in 1910, whilst the first commercial solvent-extraction process using liquid sulphur dioxide was introduced by Edeleanu at about the same time.

This was followed by various methods for the removal of mercaptans, thioethers, and disulphides in petrol by oxidation employing the so-called sweetening process using hypochlorite in alkaline solution, sodium plumbite, and copper salts, etc.

It would appear also as though the position hitherto occupied by sulphuric acid in the refining world will now be affected by the new solvent-treating method of refining, particularly in the case of lubricating oils. As in the case of wax removal, there are both single- and double-solvent processes.

Of the double-solvent type, sulphur dioxide and benzol, and also cresylic acid and propane, are in common use, whilst a number of plants are now in existence using such single solvents as furfural, phenol, liquid propane, $\beta\beta$-dichlorethyl ether (chlorex), and nitrobenzene.

The solvent treatment of oils has re-introduced the old problem of oxidation and consequent acid formation. This has resulted in a great deal of study into the inhibiting properties of certain compounds. Nevertheless, the improvements obtained in the sludging and carbonizing properties of lubricating oils, and also in their viscosity temperature relationships, more than offset any increase in the cost of manufacture as the result of having to add to them oxidation inhibitors.

Although the advances in refining methods have not been quite so spectacular as on the distillation side, largely due to the fact that experimental work in refining is usually carried out on a smaller scale in laboratories, whereas advances in distillation have evolved as the result of experiment on a more technological basis, nevertheless they have been equally as important, and have contributed just as much to the improvement of the product, as well as the lowering of the cost of such product.

In all experimental work of this kind the petroleum chemist is

handicapped by his lack of knowledge concerning the chemical constitution of the product he is attempting to improve, for whilst it is true that the chemistry of the constituents of the lower-boiling fractions of petroleum is now fairly well established, that of the higher-boiling fractions, particularly in the lubricating oil range, is practically unknown.

Synthesis.

No industry, the operations of which are based on the application of scientific principles, can be said to be developing to the fullest extent possible unless a study of synthesis is an important part of its research programme. In this respect the petroleum industry has certainly not been backward, as witness the development of the so-called "poly" plants, to quote only one example.

Although it has long been known that unsaturated hydrocarbons, no matter whether in the lower- or the higher-boiling fractions, are readily polymerized, their use on a commercial scale for this purpose is a comparatively recent development.

The production of high anti-knock spirit and the formation of aromatic liquids of even higher molecular weight from the lower olefines containing from two up to four carbon atoms in the molecule should here be mentioned.

The synthesis of lubricating oils, not only by polymerization, but also by means of the Friedel and Craft reaction, in which cyclic and chlorinated straight-chain hydrocarbons are combined in the presence of aluminium chloride is a recent development of some note. In fact during the last few years much research has been devoted towards the building up of new molecular structures.

It was not until some twenty years ago that the fundamental chemistry of the hydrocarbons awakened much interest in the petroleum industry, although in a few isolated cases investigations into this subject had been made by de la Rue, Markownikoff, Mabery, Sabatier, and Kishner.

More recently a considerable amount of work has been carried out by our contemporaries, and it would be remiss of me not to express the gratitude of the members of this Institute to them and to the larger oil companies for the public-spirited manner in which they have made themselves responsible for the bulk of this work, which has been carried out not only in their own laboratories, but elsewhere, and also for allowing the results of these investigations to be published freely, very largely through the medium of our own *Journal*.

It is probable that the increased demand, caused by the last war,

for more suitable solvents for the lacquer industry really provided the stimulus for the production of chemical intermediates and special products from petroleum, although it should be recalled that the Russian petroleum industry had been utilizing sulphonated acid sludge and naphthenic acids on an industrial scale long before 1914.

Furthermore, the development of cracking led to the production of enormous quantities of gases containing varying amounts of olefines for which a use had to be found.

In 1862 a small quantity of alcohol made from coal-gas ethylene by means of the sulphuric-acid process was exhibited at the London Exhibition, but the commercial preparation of ethyl alcohol was, until recently, entirely from molasses.

By 1920 the production of *iso*propyl alcohol from cracking gas was established on a large scale, and this was quickly followed by the preparation of ethylene glycol as an anti-freeze agent, together with many derivatives of the glycols. The chlorination of natural gasoline was the next step in development, and by 1926 the preparation of amyl alcohol and acetate had taken form. Similarly secondary butyl alcohol is being produced from butene, whilst its acetate has proved of value as a lacquer solvent.

More recently, because of the fact that propylene appears in greater quantity than *iso*butylene in cracked gases, it was thought advisable to convert it into di*iso*propyl ether by the action of sulphuric acid in order to meet the ever-increasing demand for high anti-knock fuel.

This ether has a slightly higher blending octane value than commercial *iso*-octane, and for a given tetraethyl lead concentration in corresponding blends it is also superior. Its miscibility with water and relatively low calorific value are, however, disadvantages. The latter is specially important as it is 18–20 per cent. less than that of *iso*-octane, and when the ether is present to the extent of 40 per cent. in aviation fuel, the calorific value of the latter is some 7 per cent. lower than for a similar blend with *iso*-octane.

It should be realized, however, that di*iso*propyl ether is not intended to replace *iso*-octane, but rather to augment the supply of high-octane blending material.

Developments of outstanding importance during the last few years have been the combined pyrolysis and polymerization process, whereby high-grade gasolines are now produced synthetically from both natural and cracked hydrocarbon gases, the production of benzol by high-temperature cracking, and the preparation of di-*iso*butene by the polymerization of *iso*butene in the presence of sulphuric acid.

As was to be expected, it was but a short step to the dehydrogenation of gaseous paraffins followed by the treatment of olefine–paraffin mixtures, as mentioned above. Ethane, propane, and *n*-butane can be handled to great advantage by dehydrogenation to the corresponding olefines. Of these, propylene and the butenes can be alkylated with *iso*butane or, alternatively, the butenes can be polymerized to dibutenes, which may be hydrogenated to octanes. Ethylene produced in a similar fashion may be polymerized to motor fuel. In fact, it may be stated that all the hydrocarbon constituents of natural gas may now be converted into aviation fuels with Octane Numbers (C.F.R.M.M.) of 90 and above, with the exception of methane and ethane. As these hydrocarbons are the most prolific in natural gas, it should be emphasized that their utilization is a matter of considerable urgency.

While ethane may be dehydrogenated to ethylene, which may be subsequently polymerized, the polymers produced do not yield high octane numbers on hydrogenation. Also ethylene has not yet been satisfactorily alkylated with *iso*butane in the presence of sulphuric acid on a commercial scale, but the Phillips Petroleum Company of America now effect this by thermal treatment under pressure, and in this manner produce neohexane (2 : 2-dimethylbutane).

The next step was to reduce the temperature and pressure of the polymerization processes, and catalysis has been successful in this, not only for the production of motor fuels and of lubricating oils, but also in suppressing secondary reactions whereby the polymerized olefines had a tendency to revert to hydrocarbons saturated in character.

The first mention of the polymerization of *iso*butene by means of sulphuric acid was attributed to Butlerov in 1876, and the method now in general use is effected by acid catalysts, either in the liquid phase—*e.g.*, sulphuric acid—or in the solid phase, such as orthophosphoric acid supported on a carrier, and considerable quantities of di*iso*butene are now being prepared in this manner.

In the stabilization of gasolines the *iso*butane fraction can be extracted, which, together with that found in cracking gases, represents a vast potential source of supply for the production of *iso*-octane.

The method of preparing *iso*-octane from di*iso*butene using nickel as a catalyst was first described by Edgar in 1926, but a more recent development has been the production of high-octane fuels by the hydrogenation of the condensation product from a mixture of *n*-butene and *iso*butene. In this manner one molecule of the polymer is formed from one molecule of *iso*butene, instead of from two molecules

as with di*iso*butene, thus practically doubling the yield of product for a given quantity of the branched hydrocarbon. The product on hydrogenation gives a fully saturated paraffinic fuel of 96 octane number, possessing a good lead response, and as there is always a greater proportion of normal butenes in cracked gases than *iso*butene this process is likely to take precedence.

It has been estimated that the hydrocarbon gases in the United States of America form a yearly potential supply of 9000 million gallons of polymer gasoline, including over 1000 million gallons of *iso*-octane fuel of 95–100 octane numbers. By applying these processes to waste refinery gases, an appreciable conservation of crude oil is accomplished.

The economics of these so-called "poly" plants are attractive, and appear to be of a sound profitable nature. It is no surprise therefore that polymerization plants now in operation or under construction will have an aggregate annual output exceeding 700 million Imperial gallons.

A point of interest at this stage is the number of small scale "made-to-measure" plants of the "midget" type which are being installed in many refineries.

To quote one such plant employed to process only a quarter of a million cubic feet of cracked distillate stabilizer tops daily, this yields 2800 Imperial gallons of 83–85 octane-number polymer gasoline per day. Using direct labour the plant cost £2000, and the capital cost was recovered in 36 days. The total output of the refinery was increased upon the introduction of this plant by 7 per cent.

The economic limit of polymerization plants is said to involve a feed rate of 280,000 Imperial gallons of liquid butanes and butenes giving 86,000 Imperial gallons of finished polymer gasoline per calendar day.

Rapid advance is taking place in producing any given commodity at smaller costs. Thus, according to Egloff, gasoline of 125 octane number, having 50 per cent. greater power output than present 100 octane gasolines, has been produced experimentally in petroleum laboratories. The cost per gallon of this fuel has been reduced by more than 98 per cent. due to experiments carried out over a period of one year—that is, from just over £720 to just over £10 a gallon. It is hoped that the cost may be reduced sufficiently in the near future to permit commercial production.

Although not essential for to-day's motor cars, the super-octane gasolines are a major requirement of the nation's flying forces. American refineries are now producing the world's only adequate supply of fighting-grade aviation gasoline.

It is perhaps of interest at this stage to mention that the tars

produced as by-products in a benzole pyrolysis process are themselves capable of producing good yields of 90–100 octane-number gasolines of very low freezing points by the destructive hydrogenation of the polynuclear aromatic molecules, which are the main constituents of these tars.

One cannot finish a review of these processes without discussing in greater detail those plants which use sulphuric acid as the polymerizing agent. One process of considerable importance is the polymerization of *iso*butene to di*iso*butene and then hydrogenating the dimer to *iso*-octane. The reaction is the well-known one which follows two steps: firstly absorption of *iso*butene with subsequent hydration to the tertiary alcohol, and secondly dehydration and polymerization. The concentration of the acid is of vital importance, and the time of contact is another important factor.

After absorption of *iso*butene by acid the alcohol–acid mixture is passed to a polymerization vessel and heated until polymerization is complete. When this mixture of polymers is hydrogenated over nickel, 2 : 2 : 4-trimethylpentane or the coveted *iso*-octane results.

In this respect the preparation of high-octane aviation fuel by the Sulphuric Acid Alkylation Process as put forward by A. E. Dunstan and his collaborators, as well as the Shell Group, should here be mentioned, and a thought given to the much-discussed work of Ormandy dealing with the action of strong sulphuric acid on olefines, first published in our *Journal* in 1927.

This alkylation process affects directly the union of *iso*paraffins with olefines in approximately equal volumes to form branched-chain paraffins in the presence of sulphuric acid as the catalyst and in a single-stage operation.

In this manner yields of *iso*paraffins of high-octane number are more than double those obtainable by the two-stage process of polymerization followed by hydrogenation already referred to.

Before leaving this subject, the question of isomerization should be considered. Isomerization reactions in the field of high-octane-number motor fuels have enormous potentialities.

As is well known, saturated hydrocarbons exist either as straight or branched-chain compounds, and as the latter have higher anti-knock qualities than the former in the gasoline range—an excellent example of the difference in their behaviour in an engine being *n*-heptane and *iso*-octane—considerable interest in the controlled changing of straight chains to branched chains is now being displayed by those interested in motor fuels.

To these, isomerization is important from three points of view at the moment:

(*a*) Conversion of *n*-butane into *iso*butane for use in alkylation processes.

(*b*) Conversion of *n*-pentane into *iso*pentane for use in 100 octane number aviation fuels.

(*c*) Increasing the octane number of gasolines generally.

With regard to the latter point the extension of controlled isomerisation into the broad gasoline boiling range is a problem which should receive immediate attention.

The credit for the discovery of isomerism is undoubtedly due to Dalton, who, by distilling fatty oils in 1820, prepared a gas which resembled olefiant gas but appeared to contain twice as much carbon and hydrogen in a given volume. In 1821 W. Henry prepared a similar constituent from coal gas; Faraday then isolated this constituent from the condensation products of oil gas and found that the compound contained carbon and hydrogen in the same proportion as in olefiant gas (ethylene), but had twice the density, confirming Dalton's suggestion that probably the molecules of the new gas consist of two of olefiant gas, thus giving us the first example of isomerism.

Prior to these later developments, however, an attempt had been made to produce high-octane fuels by means of cracking under more severe conditions than normally, which resulted in distillates being formed which deposited a higher proportion of gumming materials. These gumming hydrocarbons were found to be a valuable source of supply of material suitable for conversion into resins.

For this purpose certain oils are now cracked to produce distillates containing a high proportion of olefines and diolefines, both cyclic and straight chain and aromatic and substituted aromatic hydrocarbons, solely for the manufacture of synthetic resins of different colour and hardness, by means of polymerization in the presence of aluminium chloride. Such resins can be used in varnishes or converted into moulded products.

Solvents derived from petroleum have long been used in the perfume and oil-bearing-seed industries, in bone degreasing, and in the dehydration of alcohol. They have also been used as cellulose lacquer diluents, in the manufacture of printing inks, as thinners in paints and varnishes, and in various polishes, as well as for many purposes too numerous to mention.

Solvents may be derived from both the paraffin and the olefine hydrocarbons. From the saturated hydrocarbons are obtained the chloroparaffins such as methyl chloride, methylene dichloride, chloroform, and carbon tetrachloride, as well as the amyl alcohols and their

esters referred to earlier. The olefines serve as raw materials for other chlorohydrocarbons and ethers, also acetone and its homologous ketones and their products. This is no recent discovery, however, as the power of hydrocarbons with double bonds to react additively with the halogen elements was known as far back as 1795.

The chlorinated products of petroleum are also playing an important part in the preparation of extreme pressure lubricants, and the Friedel and Craft reaction, referred to earlier, for the production of synthetic lubricating oils having high viscosity index properties, from chlorine and wax and heavier oils, may assume some importance in the future, as has been the case with the specialized product known as Paraflow.

Natural gas has been playing its part in other directions, notably as a source of hydrogen and dry ice, as a result of its reaction with steam. There is no doubt, however, that alcohol production is likely to prove one of the most important industrial outlets for the utilization of natural and olefine gases and in the production of pure chemical compounds in the future.

The relative cheapness of chlorine, together with the abundance of cracking gas within recent years, have led to the production of ethylene dichloride for solvent purposes and as an important material for organic synthesis. One of its more recent important uses has been its utilization with ethylene dibromide to cause more complete expulsion of the lead from the engine after combustion when ethyl fluid is used for suppressing knock in motor spirits.

In discussing the use of chlorine, the work of E. C. Williams on the synthesis of glycerol from petroleum gases should here be considered.

The fact that trichloropropane was difficult to manufacture economically by the direct chlorination of propane, or by the further chlorination of 1 : 2-dichloropropane, has long been recognized, and therefore the hydrolysis of 1 : 2 : 3-trichloropropane was considered out of the question.

However, the direct substitution of chlorine into the propylene molecule in such a way that the unsaturated bond remains unaffected has led to a method of synthesis of allyl chloride, which may then be transformed to glycerol by three alternative processes: either conversion to 1 : 2 : 3-trichloropropane by the addition of chlorine, or to dichlorohydrin by chlorohydrination, or by preliminary hydrolysis to allyl alcohol followed by chlorohydrination to glycerol monochlorohydrin.

The production of synthetic rubber from such materials as 1 : 3-butadiene prepared from the dichloride of butane, and isoprene prepared from the dichloride of *iso*pentane, is also once more receiving attention.

Despite the advances, of necessity so briefly recorded in this address, the production of chemical intermediates from petroleum is but still in its infancy, and it is only by organized research, not necessarily with a view to immediate financial gain, that we can hope to advance our knowledge in this respect.

It should also be borne in mind, to quote only one case, that the method of manufacture whereby the cost of *iso*-octane was reduced from £5 to well below 2*s*. a gallon has been perfected within the last three years. Triptane (2 : 2 : 3-trimethyl butane), which is believed to have anti-knock properties even better than those of neo-hexane, and has so far been prepared by the hydrogenation of the olefine formed by the dehydration of 2 : 2 : 3-trimethyl butanol-3, is a discovery which has been made only within this last twelve months.

Petroleum consists essentially of compounds formed from two elements only, carbon and hydrogen. Carbon is the key element of organic nature, and any organic compounds capable of being synthesized in the laboratory should be capable also of being produced from petroleum. The value of research to the future of industry and to the industrial life of the nation cannot be over-estimated, and at the present time research is of greater necessity than ever, particularly when the nation is engaged in a scientific war. Such research should be of a wider scope than that of any of the Government Departments, the outlook of whose scientific staffs is often limited to their own special problems.

Research in petroleum science is being intensively carried out throughout the world, particularly in enemy territory where the whole of the scientifically trained men still remaining have been organized and are fully employed in professional work.

In this country, it is equally necessary that the whole of the scientific knowledge available, both of teams of laboratory workers and of individual scientific workers, should be fully employed, mainly on problems whose solution is necessary for ultimate victory over the enemy, but not neglecting the fundamental research essential to ensure that at the end of the war our industries are able to compete on favourable terms with all other countries.

To those who have done me the honour of reading this address I recommend these latter remarks for their earnest consideration.

SOLUBILITY OF CRACKED RESIDUES IN SOME SOLVENTS.

By J. Voskuil.

Synopsis.

When cracked residue and fuel oil containing this product are diluted with different quantities of a precipitant hydrocarbon, and the percentages of precipitate are plotted against the dilution, "precipitation curves" are obtained. These lines are practically horizontal at high dilutions of aliphatic hydrocarbons and for *cyclo*hexane. When adding large amounts of benzene to a cracked residue not containing sludge, a certain amount of precipitate is also formed. This precipitation curve is also horizontal at high dilutions. In the presence of sludge, small quantities of benzene may peptize part of the sludge, whereas larger quantities may again increase the amount of the precipitate; so a minimum in the curve is formed. This is illustrated by an example.

The results of these experiments were used to make a study of the effects when a cracked residue or fuel is extracted with pure benzene (for instance, in the Sediment-by-Extraction Test).

This led to the conclusion that the amount of the sediment after the extraction is dependent on the viscosity of the cracked residue or fuel and on the sizes of the pores in the extraction thimble.

In the second part of this article a comparison is made between the percentages benzene-insoluble in residues highly diluted with benzene and after a Soxhlet extraction of the pentane-insoluble with solvents increasing in solvent power up to benzene.

The extraction method gives higher values than the dilution method. It is thought that the constituents which stay in solution with even great quantities of benzene are precipitated with pentane and lose their solubility in benzene during the step-by-step extraction in which the adsorbed protective layers are removed.

The colloid-chemical nature of the cracked residue is clearly demonstrated by this.

Introduction.

In a previous publication [1] an investigation into the formation of precipitate in cracked residue and fuel oil containing this product, when increasing quantities of a precipitant hydrocarbon—*e.g.*, 60/80 gasoline were added—was reported. By plotting the quantity of precipitate as function of the dilution, "precipitation curves" were obtained. An extrapolation of these precipitation curves to zero dilution gave the quantity of "sludge"—*i.e.*, flocculated asphaltenes, etc.—which could not be kept in solution owing to the insufficient solvent power of the product.

In the above publication mention was also made of the application of gasoline–benzene mixtures to "flatten out" the precipitation curves so as to simplify the extrapolation.

The present publication describes the results of the continued investigation into the shape of the precipitation curves and the solubility of cracked residues in some solvents frequently applied in practice.

Solvents Used.

In Table I the solvents are given, together with some physical properties. The solubility of Dubbs residue in these solvents increases from pentane to benzene in the order shown.

Table I.

Specific Gravity and Refraction of the Solvents Used.

Solvent.	Sp. gr. 20/4.	Refractive index, 20° C.	Details.
Pentane	0·6257	1·3575	Made from topped gasoline. Contains about 12% of *iso*pentane.
60/80 Gasoline (I.P.T. Petroleum Spirit)	0·6847	1·3850	Mixture of *n*-hexane, *iso*heptane, and some naphthenes.
*cyclo*Hexane	0·7785	1·4263	Obtained from hydrogenated benzene chemically pure.
Carbon tetrachloride	1·595	1·4630	Commercial product; chemically pure.
Benzene	0·8755	1·4990	Chemically pure, free from thiophene.

Plotting of the Precipitation Curves.

In theory the procedure is very simple: the residue is diluted with a certain volume of the precipitant liquid per gram of residue, and the resultant quantity of precipitate is then determined. In practice, however, great difficulties are encountered.

In the first place, the mixtures cannot be filtered, so that they have to be centrifuged. In his experiments the author used a series centrifuge from the International Equipment Co., Boston, U.S.A., with A.S.T.M., long-tapered bottom centrifuge tubes. These tubes were used in two sizes: 50 ml. for low dilutions and 100 ml. for high dilutions.

The centrifuge could develop a velocity of 3000 r.p.m. with the 50-ml. tubes and of 1800 r.p.m. with the 100-ml. tubes. The radius from the centre to the middle of the tube was 21 cm.

The centrifuging was continued until there was a distinct boundary line between precipitate and supernatant liquid, which did not shift in position on continued centrifuging. The precipitates were then washed out and rinsed with carbon disulphide into weighed gum dishes (I.P.T. G. 25 (T)). The percentage of precipitate was found by re-weighing the dishes after evaporation of the carbon disulphide and drying of the precipitate in an oven at 110° C.

Another difficulty was experienced in washing out, since the precipitate entrained an appreciable quantity of the medium, from which a fresh quantity of precipitate was formed when washing with the precipitant liquid. In the previous article [1] this wash-error was eliminated by using the so-called correction formula:

$$g = \frac{AE(1+x) - \frac{ETV}{100}}{E(1+x) + A - V - \frac{ET}{100}};$$

g = weight of precipitate to be determined;
A = weight of precipitate to be obtained;
E = weight of residue employed;
x = degree of dilution (with a dilution 1 : 1, $x = 1$; for 1 : 2, $x = 2$, etc.);
T = percentage of precipitate at very high dilution;
V = volume of precipitate in centrifuge tube.

The correction formula is based on the assumption that the specific gravities of cracked residues and of precipitates are equal, or approximately equal, to 1. Generally this may be taken to be sufficiently correct, but with mixtures of residue and gas oil with a high proportion of gas oil this may not be the case, and the formula was accordingly modified so as to make allowance for the specific gravity.

When in the derivation of the formula the specific gravity of the residue or mixture (d_1) and that of the precipitate (d_2) are taken into account:

$$g = \frac{AE\left(\frac{1}{d_1} + x\right) - \frac{ETV}{100}}{E\left(\frac{1}{d_1} + x\right) + \frac{A}{d_2} - V - \frac{ET}{100 \,.\, d_2}}$$

Accuracy of the Results.

It is of importance to know what value can be attached to the results obtained. The correction is the greatest at low dilutions or if the sludge can be centrifuged off at once because the residue or fuel oil has a sufficiently low viscosity (dilution 1 : 0).

It can be calculated that the absolute accuracy in the extrapolated sludge values is 3–4 units in the first decimal place. It follows from this that the accuracy is greater with high than with low sludge values.

Precipitation Curves with 60/80 Gasoline, Benzene and Mixtures of These.

A mixture of a cracked residue A and a gas-oil with a sludge content of 3·4 per cent. was diluted with different percentages of 60/80 gasoline,

Table II.

Relation between the Percentage of Precipitate in the Residue A—Gas Oil Mixture and the Dilution with 60/80 Gasoline and Mixtures of this with Benzene.

Dilution.	60/80 gasoline.	90 gasoline, 10 benzene.	80 gasoline, 20 benzene.	70 gasoline, 30 benzene.	60 gasoline, 40 benzene.	50 gasoline, 50 benzene.	60 gasoline, 40 benzene.	30 gasoline, 70 benzene.	20 gasoline, 80 benzene.	10 gasoline, 90 benzene.	Benzene.
1 : ¼	4·3	4·1	4·0	3·6	3·4	3·1	2·8	2·5	2·1	1·8	*1·6
1 : ½	5·3	4·4	4·3	3·7	3·4	2·9	2·6	2·1	1·5	1·3	0·9
1 : 1	6·1	5·1	4·8	4·0	3·4	2·8	2·1	1·5	0·9	0·5	0·14
1 : 2	7·0	5·8	5·1	4·2	3·5	2·9	2·0	1·3	0·6	0·5	0·12
1 : 3	—	—	—	—	—	—	—	1·4	0·6	0·4	0·14
1 : 4	—	—	—	—	—	—	—	—	—	0·5	0·16
1 : 10	—	—	—	—	—	—	—	—	—	—	0·7
1 : 20	—	—	—	—	—	—	—	—	—	—	1·3
1 : 40	—	—	—	—	—	—	—	—	—	—	1·5
1 : 100	8·8	6·9	5·9	5·0	4·3	3·7	3·1	2·5	1·8	1·8	1·6

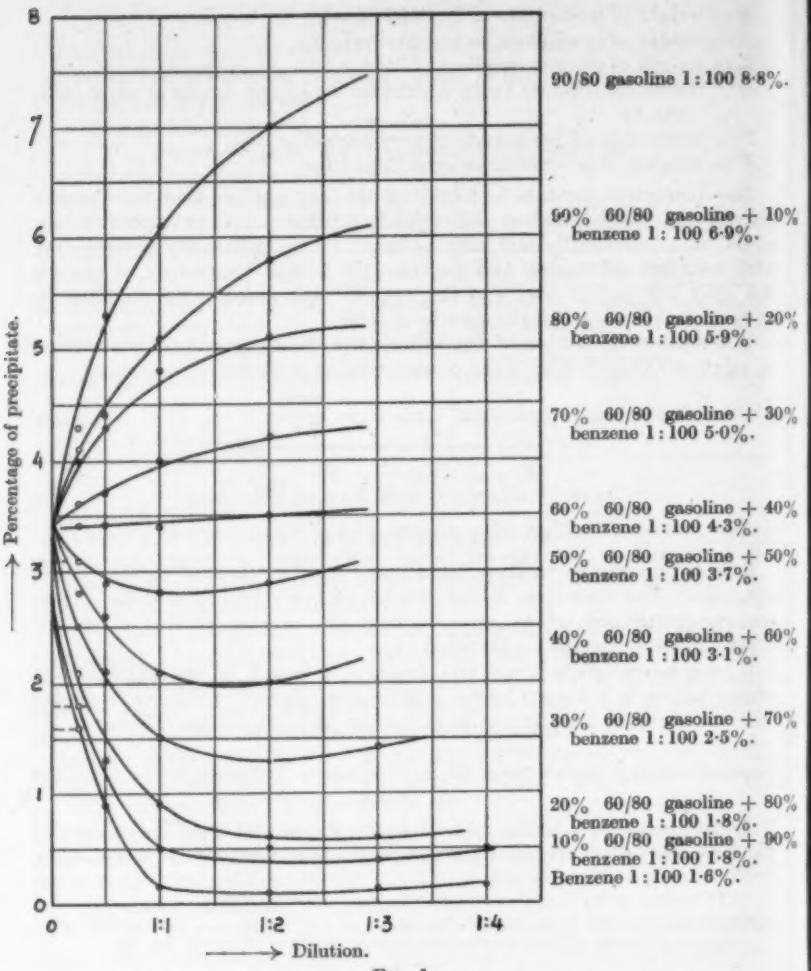

Percentage of precipitate.
0
1
2
3
4
5
6
7
8
0
1:1
1:2
1:3
1:4
Dilution.
90/80 gasoline 1 : 100 8·8%.
99% 60/80 gasoline + 10% benzene 1 : 100 6·9%.
80% 60/80 gasoline + 20% benzene 1 : 100 5·9%.
70% 60/80 gasoline + 30% benzene 1 : 100 5·0%.
60% 60/80 gasoline + 40% benzene 1 : 100 4·3%.
50% 60/80 gasoline + 50% benzene 1 : 100 3·7%.
40% 60/80 gasoline + 60% benzene 1 : 100 3·1%.
30% 60/80 gasoline + 70% benzene 1 : 100 2·5%.
20% 60/80 gasoline + 80% benzene 1 : 100 1·8%.
10% 60/80 gasoline + 90% benzene 1 : 100 1·8%.
Benzene 1 : 100 1·6%.

FIG. 1.

PRECIPITATION CURVES OBTAINED WITH 60/80 GASOLINE, BENZENE AND MIXTURES OF THESE PRODUCTS IN A MIXTURE OF CRACKED RESIDUE A WITH GAS OIL (40%).

benzene and mixtures of these. The resulting percentages of precipitate have been given in Table II and the precipitation curves in Fig. 1.

The precipitates had, of course, to be washed with 60/80 gasoline, as otherwise the first part of some of the curves would be similar to the dotted lines drawn in Fig. 1. Washing with the precipitant itself would be permissible only in those cases in which the content of precipitate at high degrees of dilution would be higher than the sludge content.

It is interesting to note that with the mixture 50 per cent. of 60/80 gasoline and 50 per cent. of benzene a minimum occurs in the precipitation curves. This minimum becomes more pronounced with increasing percentages of benzene in the mixture.

The effect of the benzene on the sludge is interesting. At a definite dilution there is a maximum solubility of the sludge in the medium. When more benzene is added, more precipitate is formed, reaching with infinite dilution a certain limit, just as it did with 60/80 gasoline. The obvious question now arising is whether every cracked residue, even one containing no sludge at all, behaves similarly. This is actually found to be the case. Every Dubbs residue examined by the author produces asymptotically more precipitate with increasing quantities of benzene. A minimum is, of course, absent in the case where there is no sludge. The maximum stability of a system without sludge would have to be determined by some other means.

*cyclo*Hexane as Precipitant.

*cyclo*Hexane is a precipitant which flattens out the curves and, as we know by experience, gives no minima. The results have been collected in Table III; the percentages practically coincide with those obtained with mixtures of 70 per cent. of 60/80 gasoline and 30 per cent. of benzene and which are plotted in Fig. 1.

Table III.

Relation between the Percentage of Precipitate in the Residue A—Gas-Oil Mixture and the Dilution with cyclo*Hexane.*

Dilution.	Percentage of precipitate.
1 : $\frac{1}{4}$	3·6
1 : $\frac{1}{2}$	3·8
1 : 1	3·9
1 : 2	4·3
1 : 100	5·5

Table IV gives the percentages of precipitate obtained with *cyclo*hexane in different dilutions in some cracked residues. The results have been plotted in Fig. 2.

Table IV.

Relation between the Percentage of Precipitate in Some Residues and the Dilution with cyclo*Hexane.*

Dilution.	Residue *B.*	Residue *A.*	Residue *C.*	Residue *D.*	Residue *E.*	Residue *F.*
1 : 1	16·0%	4·0%	2·2%	0·5%	0·2%	0·2%
1 : 2	17·0	5·3	3·0	0·6	3·5	3·0
1 : 3	18·1	6·2	3·5	—	5·1	4·2
1 : 5	—	7·3	4·1	1·3	6·6	5·5
1 : 100	19·6	9·0	4·9	3·2	8·4	7·5

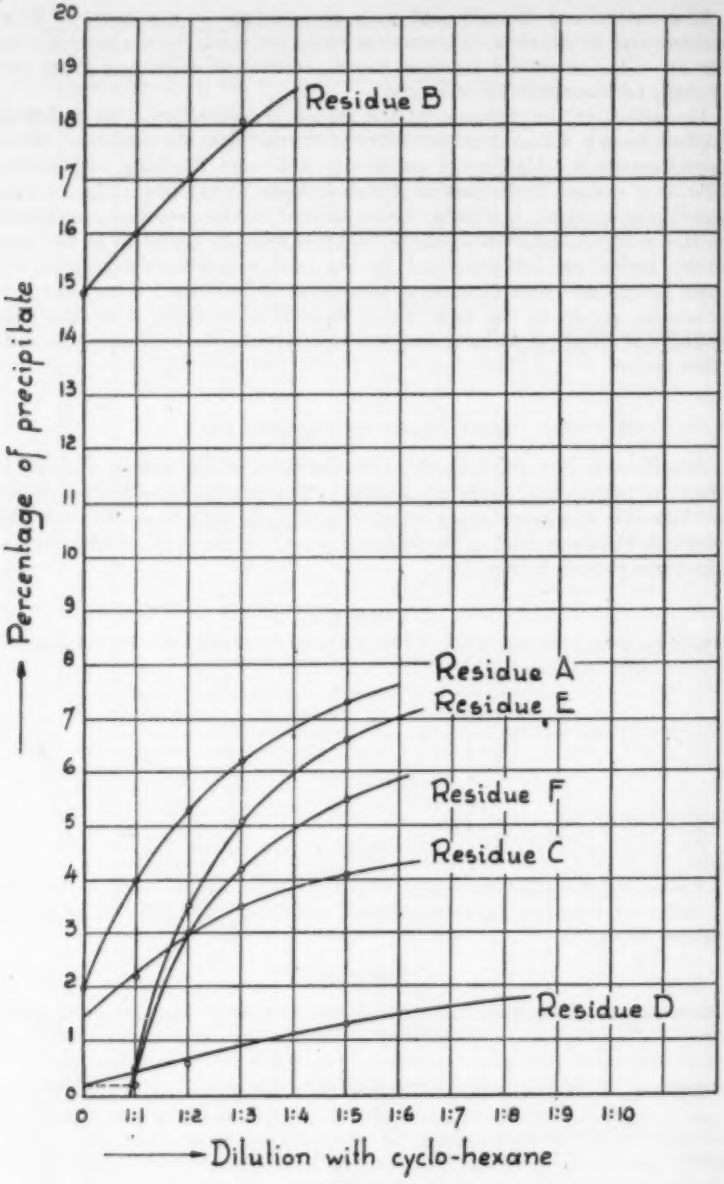


FIG. 2.

PRECIPITATION CURVES OBTAINED WITH *cyclo*HEXANE IN A FEW CRACKED RESIDUES.

Residue *B* was a strongly cracked residue. The residues *E* and *F* were two cracked residues which could be mixed with 10–20 per cent. of P.D. bottoms without giving any difficulty in the preheaters; these are cases in which a "threshold value" was found for the formation of precipitate in cracked residue by dilution. Under the microscope, with dark-field illumination, inhomogeneities such as inorganic and carbon-like material were, indeed, noticeable, but the quantity was so small as to defy determination. It was roughly estimated to be less than 0·1 per cent. Strictly speaking, these curves of the residues *E* and *F* should not end in the *X* axis, but should run horizontally to the *Y* axis from about 0·1 per cent. (see dotted line).

The following is also worth mentioning:

In practice Residue *C* was found to be less stable towards heating than Residue *A*, although the former contains less sludge; its precipitation curve is flatter than that of *A*.

The Extraction of a Residue with Pure Benzene.

The behaviour of benzene towards cracked residues and blends is of practical importance because it explains the phenomena encountered when carrying out, for instance, the Sediment-by-Extraction Test, (A.S.T.M. Designation D473–38T).

Suppose that a residue or blend (*e.g.*, the mixture of Residue *A* with gas oil) is subjected to the Sediment-by-Extraction Test.

Owing to its comparatively high viscosity, this fuel does not pass through the pores of the alundum thimble. If benzene condenses in the thimble, the composition of the fuel–benzene mixture will shift to the right along the *X* axis (see Fig. 1). If, for instance, the viscosity of the 1 : 2 mixture is such that it can pass through the pores of the alundum thimble, it will be clear that practically no precipitate is left behind.

At the bottom of the extractor, however, precipitate is deposited owing to the excess of benzene, a symptom that has frequently been noticed previously.

The quantity of sediment obtained in this test therefore depends on the pore size of the alundum thimble and the viscosity of the fuel.

Soxhlet Extraction with Solvents Increasing in Solvent Power.

It is different when the extraction is carried out successively with solvents increasing in solvent power. This takes place in the examination of asphaltic bitumen in the Soxhlet apparatus. Hillman and Barnett have reported on this in their publication on an investigation into cracked and uncracked asphaltic bitumens.[2]

Hillman and Barnett separate asphaltic bitumen by means of *iso*pentane into a solid and a liquid part (pentane-asphaltenes and pentane-maltenes). They next extract the pentane-asphaltenes successively with *iso*pentane, hexane, carbon tetrachloride, benzene, carbon disulphide, and pyridine in a Soxhlet apparatus. The influence of the medium on, for instance, the benzene-insoluble is eliminated here by a gradual removal of the "lighter"

constituents, which, in combination with the benzene, have a maximum solvent power for the benzene-insoluble.

According to an unpublished statement of Hillman and Barnett, the percentage of carbon tetrachloride-insoluble is higher if the extraction with hexane is not immediately followed by that with carbon tetrachloride, but with mixtures of hexane and carbon tetrachloride, each time containing 10 per cent. more of the latter substance.

Comparison of the Quantity of Benzene-insoluble after the Soxhlet Extraction and after High Dilution.

It has been ascertained that the quantities of benzene-insoluble in high benzene dilution and after the modified Soxhlet extraction described above are the same. One would expect this, as the influence of the medium on the benzene-insoluble is eliminated in both methods.

Table V gives the quantities of benzene-insoluble in some residues with the dilution method and after the Soxhlet extraction.

Table V.

Percentage of Benzene-insoluble with the Soxhlet Extraction and with the Dilution Method.

Residue.	Percentage insoluble in pentane.	Percentage insoluble in benzene (Soxhlet extraction).	Percentage insoluble in benzene (high dilution).
A . . .	16·2	6·5	2·3
C . . .	8·7	2·0	0·6
D . . .	10·0	2·9	0·4
E . . .	15·1	4·8	0·6
H . . .	19·2	8·7	1·8
K . . .	20·1	10·4	2·3

Table VI.

Experiments with Residue A.

Percentage benzene-insoluble in accordance with the dilution method.		Percentage benzene-insoluble in accordance with the Soxhlet extraction.	
(*a*) Dilution 1 : 100 . . .	2·3%	(*d*) At condensation temperature of the solvent . . .	6·4%
Dilution 1 : 1000 . . .	2·4%	At room temperature ("cold extraction") . . .	7·7%
(*b*) Dilution 1 : 100 after precipitation of the pentane insoluble *without* drying of the precipitate . . .	2·6%	(*e*) Extraction in carbon dioxide atmosphere . . .	5·9%
(*c*) Ditto with drying of the pentane-insoluble (18 hrs. at 110° C.)	2·9%	(*f*) Extraction with exclusion of light	5·7%
		(*g*) Extraction with 60/80 gasoline–benzene mixtures (rising by 5%) . . .	4·9%

TABLE VII.

Shaking-out of the Pentane Precipitate with Solvents.

(*a*) Successively shaking-out of the pentane-precipitate with a large excess of 60/80 gasoline–benzene mixtures (rising by 5%) *without* drying of the precipitate	4·4%
(*b*) Ditto with drying of the pentane precipitate	5·5%
(*c*) Ditto with gasoline–CCl_4 mixtures and with benzene	5·8%

There is a remarkable difference in benzene-insoluble between the extraction and the dilution method, the results of the latter being much lower.

To account for this great difference, the author experimented further with Residue *A*.

The idea was to vary several factors (such as drying of the pentane precipitate, influence of light and oxygen, etc.) which might influence the results of the dilution and the extraction method. The results of these experiments have been collected in Tables VI and VII.

Experiments with the Dilution Method.

(*a*) In the first place it was ascertained whether 1 : 100 was a sufficient dilution. To this end the percentage of precipitate was determined at a dilution of 1 : 1000. The increase of 0·1 per cent. (2·3–2·4 per cent., *a*, Table VI) is practically negligible. In point of fact we had already found that, in a 1 : 100 dilution, every cracked residue is on the asymptotic part of the precipitation curve.

(*b*) It had occurred to us that the previous precipitation and drying of the pentane-insoluble might cause such changes in the precipitate as to render part of it insoluble in benzene. The drying was first eliminated by at once taking up the filtered pentane precipitate in excess benzene. Although this gave an increase of 0·3 per cent., the value for the benzene-insoluble was still far below 6·4 per cent.

(*c*) The influence of drying was ascertained by drying the pentane precipitate for 18 hours at 110° C. By this manipulation the value was slightly increased to 2·9 per cent.

Experiments with the Extraction Method.

(*d*) It might be that normal extraction at the rather high condensation temperature of the solvents could effect polymerization or the like of the residue constituents, causing these to become less and less soluble.

If so, extraction at room temperature should give lower results. This "cold extraction" was carried out as follows (see Fig. 3):—

The separating funnel *A* containing the extraction liquid was connected by means of a glass tube with drain-cock *F*, with a wide glass filter *B*, which contained a Jena Glass filter *G* 3 (*C*) with the precipitate. *A* was heated by an electric heating ring *D*. The solvent vapours consequently condensed in the condenser *E* and the liquid regularly dripped into *C*. Extract plus solvent were conducted back to *A* through the glass tube.

After the cold extraction the percentage benzene-insoluble was 7·7 per cent., hence *higher* than after the Soxhlet extraction. Also in cold ex-

tractions with the other residues the percentages of benzene-insoluble were either higher than or equal to those after the Soxhlet extraction. The high temperature was consequently not responsible for the great difference between the dilution method and the extraction method.

(*e*) The possible influence of oxygen on the precipitate (oxidation polymerization) was next considered, as during the long time required by the Soxhlet extraction the precipitate has ample opportunity of being oxidized. An extraction carried out in a current of carbon dioxide actually gave a lower result: 5·9 per cent., but this was still much higher than that of the dilution method.

(*f*) The percentage of benzene-insoluble was not radically altered

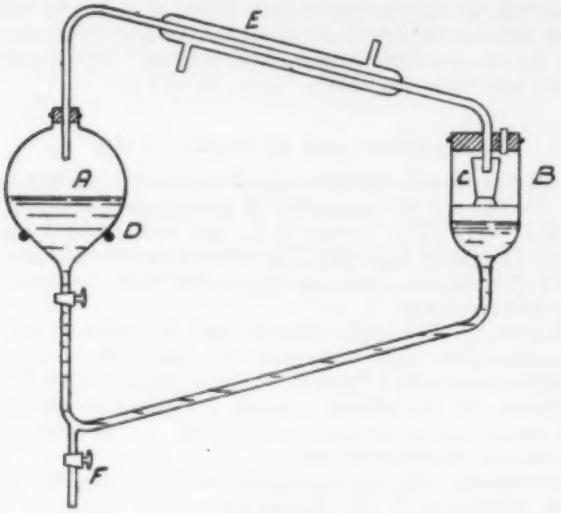


FIG. 3.

EXTRACTION APPARATUS.

by the influence of light. An extraction carried out in the dark gave a result of 5·7 per cent.

(*g*) Carbon tetrachloride is known to react with a number of substances (bituminous substances among them) under the influence of light, splitting off HCl.[3, 4]

A well-known example of this is the decomposition of CCl_4 in the presence of iron. When a little aniline is boiled with CCl_4 under a reflux condenser in diffused daylight, hydrochloric acid can be distinctly detected after half an hour.

Dubbs residue and "asphaltenes" also gave a positive chlorine reaction after being boiled with CCl_4 for half an hour under a reflux condenser. As liberated chlorine and chlorine compounds cause such changes in residues as to render them less soluble (coagulation, polymerization), it is natural

to assume that the great difference between extraction and dilution method might be due to the use of CCl_4. An extraction was therefore made without CCl_4.

If CCl_4 is omitted, the extraction wth 60/80 gasoline should be followed by extraction with mixtures of 60/80 gasoline and increasing quantities of benzene (rising by 5 per cent.), and finally with pure benzene. By this procedure the author obtained 4·9 per cent. of benzene-insoluble—*i.e.*, 1·5 per cent. lower than after extraction with CCl_4.

This effect is, however, incapable of accounting for the difference from the dilution method, which is still large.

The only explanation left was to assume that the effect of step-by-step removal of the protection round the pentane precipitate so as to eliminate the influence of the soluble on the insoluble part differs fundamentally from the application of a high dilution to attain the same purpose.

This was further demonstrated by the following two experiments:

(1) *Shaking out of the pentane precipitate with solvents of an increasing solvent power.*

(2) *Mixing experiments.*

(1) *Shaking out the Pentane Precipitate with Solvents.*

(a) *With Gasoline–Benzene Mixtures.*—This manipulation may be considered as intermediate between the dilution and the extraction method.

The residue was weighed into the centrifuge tubes and diluted with 100 × its volume of pentane. The pentane precipitate centrifuged off was thoroughly washed a few times with pentane until the wash liquid was almost colourless. The precipitate was subsequently mixed with 60/80 gasoline and the above manipulations were repeated. The gasoline was replaced by a mixture of 95 per cent. 60/80 gasoline and 5 per cent. benzene, and so on, ending with pure benzene. The benzene-insoluble was then rinsed out with CS_2 into a weighed gum dish; after evaporation of the CS_2 the precipitate was dried and weighed. The percentage insoluble was 4·4 per cent. (*a*, Table VII).

This shows that the shaking method gives a final result very close to that obtained in the extraction method with gasoline–benzene mixtures.

(*b*) A previous drying of the pentane asphalthenes immediately caused this figure to rise to 5·5 per cent. (*b*, Table VII).

(*c*) The influence of CCl_4 on the shaking method was also ascertained. The residue was shaken first with 60/80 gasoline and subsequently with mixtures of 60/80 gasoline and CCl_4. As the mixture with 80 per cent. of CCl_4 did not separate in the centrifuge owing to the slight difference in specific gravity between precipitate and liquid, the precipitate obtained after centrifuging with 70 per cent. of CCl_4 and 30 per cent. of 60/80 gasoline and washing out was mixed with pure CCl_4. This precipitate was suspended in the CCl_4 by shaking, part of it dissolved, and the insoluble part then had a structure which allowed it to be filtered off in a Jena-glass filter G 4. The residue on the filter was thoroughly washed with CCl_4, then rinsed quantitatively into the centrifuging tube and shaken out with benzene. In spite of the fact that a few stages had been skipped in the shaking

process, and that a slight loss might have occurred in rinsing the CCl_4 precipitate into the centrifuge tube, the percentages of benzene-insoluble now amounted to 5·8 per cent. (*c*, Table VII).

(2) *Mixing Experiments.*

Residue *A* was mixed in different concentrations with a straight-run residue of an "aromatic" type and with pyridine. The percentage benzene-insoluble in the mixtures was determined with the dilution and with the extraction method. The results are collected in Table VIII and in Fig. 4.

TABLE VIII.

Percentages of Benzene-insoluble in Mixtures of Residue A *with a Straight-run Residue and with Pyridine according to the Extraction and the Dilution Methods.*

Mixture.	Extraction.	Dilution.	Mixture.	Extraction.	Dilution.
100% residue *A*	6·4%	2·3%	100% residue *A*	6·4%	2·3%
80% res. *A* + 20% str.-run res.	6·0	1·0	80% res. *A* + 20% pyridine	5·4	1·3
60% " + 40% " "	5·2	0·4	80% " + 40% "	3·9	0·89
40% " + 60% " "	—	0·3	40% " + 60% "	2·6	0·59
30% " + 70% " "	3·8	—	30% " + 70% "	—	—
20% " + 80% " "	—	0·1	20% " + 80% "	1·3	0·23
100% straight-run residue	2·8	0·09	100% pyridine	0	0

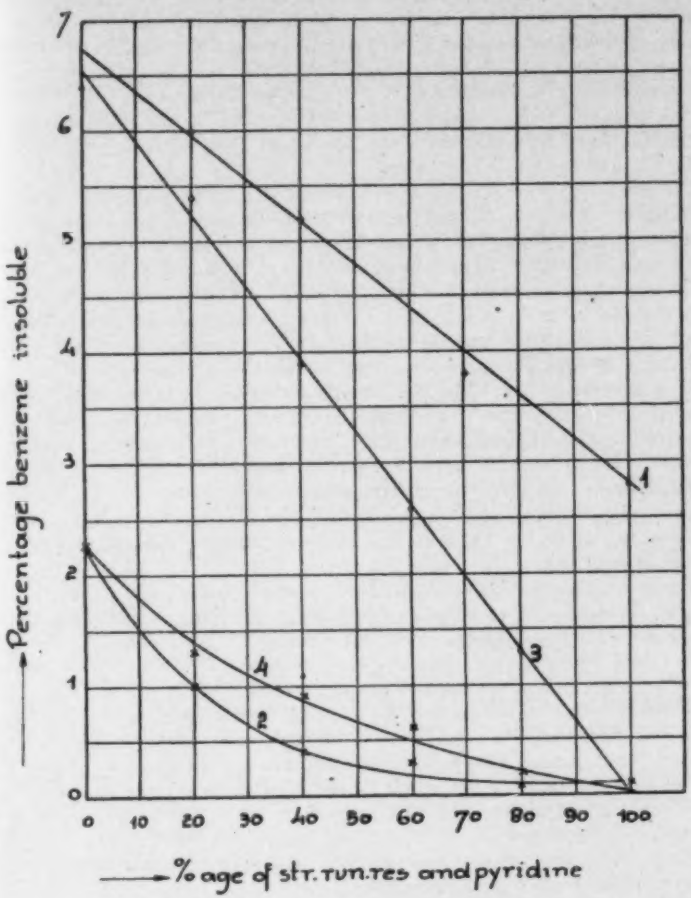
When plotted, the quantities of benzene-insoluble as a function of the mixing ratio give a straight line in the extraction method (Fig. 4, the straight lines 1 and 3); in the dilution method *curves* are obtained (Fig. 4, curves 2 and 4). In the latter method the percentage insoluble is invariably lower than the theoretical quantity. This discrepancy is more pronounced with the straight-run residue than with the pyridine mixture.

Theoretical Considerations.

In the previous publication [1] it was stated that the compounds of straight-run and cracked residues insoluble in aromatic-free gasoline, the so-called "asphaltenes," form a large series of products with varying solubility in organic media. According to the publication of Pfeiffer and van Doormaal [5] the asphaltenes of bitumens dissolve or peptize better in non-polar organic liquids of a hydro-aromatic or aromatic nature than in aliphatic ones, and especially the high-molecular aromatics favour the peptization of the asphaltenes.

It will be clear that the different curves represented in Fig. 1 obtained by diluting the mixture of cracked residue *A* and a gas-oil with increasing quantities of several gasoline–benzene mixtures illustrate the relation between the aromatic content of the solvent and its solvent power on the "asphaltenes" of this residue. It appears that the solvent power of *cyclo*hexane is about the same as that of a mixture of 70 per cent. of gasoline and 30 per cent. of benzene. As the amount of insoluble substances in these liquids is still higher than the sludge present in the fuel, we must assume that the other components of this fuel have a still better dissolving power upon its asphaltenes; it could be compared with that of a mixture of, say, 58 per cent. of gasoline and 42 per cent. of benzene. This mixture

may therefore be regarded as the "neutral washing liquid" for the sludge, as was described in the previous publication,[1] p. 189.



1 Extraction of residue A-str. run. res. mixtures.
2 Dilution " " " "
3 Extraction of residue A-pyridine mixtures.
4 Dilution " " "

FIG. 4.

THE PERCENTAGES OF BENZENE INSOLUBLE IN MIXTURES OF RESIDUE A WITH A STRAIGHT-RUN RESIDUE AND WITH PYRIDINE ACCORDING TO THE EXTRACTION AND THE DILUTION METHOD.

The increasing amounts of precipitate formed when employing increasing amounts of these solvents with less dissolving power than the maltenes

must be explained by the decreasing influence of the maltenes in the higher dilutions. The same reasoning can be applied to explain the decreasing amount of the sludge with small quantities of better peptizing solvents (mixtures containing more benzene). With further increasing quantities of highly aromatic solvent of low molecular weight a complication occurs, for the amount of precipitate again increases. It is probable that in these mixtures the concentration of certain peptizing constituents present in the original residues—for instance, high molecular components with an aromatic character—decreases too much, so that these substances lose their efficiency.

To make our reasoning clear we should like to mention the following working hypothesis. We may imagine the asphaltene micellae in a cracked residue without sludge to be built up of nuclei with a high C : H ratio (aromatic), surrounded by successive layers of high-molecular components with a gradual decrease in the C : H ratio. These mantles, which are supposed to be more or less diffuse, form a kind of continuous transition from the asphaltene micella nucleus to the continuous phase. Low-molecular, mobile molecules would not be suitable mantle substances.

If a material of this type is diluted with an aliphatic hydrocarbon the nature of the continuous phase is altered; no continuous transition between the continuous and the disperse phases can now be formed by the available mantle substances, and more or less complete separation of the disperse phase follows. If a solvent rich in aromatics is added to a cracked fuel already containing sludge, hence a fuel with a shortage of mantle substances, the difference between the phases is smaller; thus the flocculated sludge is peptized.

We must imagine the formation of the mantle round the nuclei to be a sort of adsorption process, as an increase of the quantity of solvent shifts the adsorption equilibrium and cause gradual "dismantling," owing to which part of the disperse phase is precipitated. This working hypothesis may serve to explain the asymptotic precipitation curve.

When the insoluble components of a cracked residue are precipitated with pentane, and the precipitate is filtered off and treated with a large quantity of benzene, practically the same amount of insoluble material is found as when treating the original residue with this amount of benzene. This experiment shows that the pentane maltenes show no, or only a very small, peptizing effect in benzene solutions. If, however, the precipitate with pentane is extracted with solvents of increasing aromatic content (gasoline–benzene mixtures), the total amount of substances insoluble in benzene increases, showing that that part of the asphaltenes which is soluble in these mixtures is necessary to peptize part of the material in itself insoluble in benzene; these fractions of the asphaltenes must be regarded as the mantle substances of the cracked nuclei in the solution in benzene. It will now be clear that from the amount of benzene insoluble after the extraction in our mixing experiments (Table VIII) a mathematical relationship could be found between the dilution and the amount of benzene-insoluble material, because all the nuclei and their mantles were precipitated with pentane, and after that the mantles were quantitatively removed. In the dilution experiments, however, these protective bodies remain present, but their influence cannot be expressed in a simple

mathematical equation with the mixing proportion, as the adsorption equilibrium now also plays a part. For actual practice the most valuable criteria are the amount of sludge present in a fuel without dilution (extrapolated sludge value) and the changes of this quantity upon blending or heating; the experiments described, however, displayed the colloid chemical nature of Dubbs residue.

ACKNOWLEDGMENT.

The author wishes to express his thanks to the Management of the Bataafsche Petroleum Maatschappij for their kind permission to publish the foregoing.

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THE CATALYTIC EFFECT OF METALS ON THE AGEING OF LUBRICATING OIL FOR DIESEL ENGINES.*

By H. L. Matthijsen †

During the examination at regular intervals of the used lubricating oils from the Maybach engines of the triple car-Diesel trains belonging to the Netherlands Railways, the question was raised as to whether the small metal splinters present in the used oil and also the cylinder-wall, the piston-rings, etc., might be able to increase or reduce the content of oxidation- or ageing-products.

Many references to the effect of metals, etc., on ageing are to be found in the literature [5, 8, 16, 21, 26, 31, 32, 33, 35, 36, 37, 42], but on the whole they are so vague that we have found it necessary to test this point ourselves.

As it was not possible to carry out such work in the engines of the diesel trains, the experiments were made in a laboratory oxidation instrument designed by Mr. A. Mollinger, Mech. Eng., a lecturer at the Technical High School at Delft, Mechanics Section.

We have learned from an elaborate study of the relevant literature of recent years on the ageing of lubricating oil [2, 3, 4, 5, 6, 7, 8, 10, 14, 21, 22, 24, 27, 28, 29, 32, 38, 39, 41], that twenty-three different laboratory oxidation methods have been worked out.

The B.A.M. Test and the Indiana oxidation test were preferred some time ago in the English-speaking countries, but during the past year the simple dish method has become popular and found favour with the Bureau of Standards. The Sligh test, which the A.S.T.M. at first recommended,[29] has recently declined in favour. France, Italy and Germany, moreover, each have methods of their own.[6, 22, 4]

Although a good many articles make mention of satisfactory correlation between the engine tests and some or other oxidation test, considerable uncertainty still prevails, and many still hold the view that oxidation tests can never give conclusive evidence as to the quality of a lubricant in practice (cf.[17]).

Our principal object being to determine the catalytic effect of metals on ageing, and not the quality of the lubricating oil in practice, we are publishing these results in the hope that they may contribute something towards a better understanding of the decisive factors governing the ageing of lubricating oils. Figs. 1 and 2 represent the oxidation instrument, designed by Mollinger.

100 grams of the oil under test are put into a sheet-iron tank, after which

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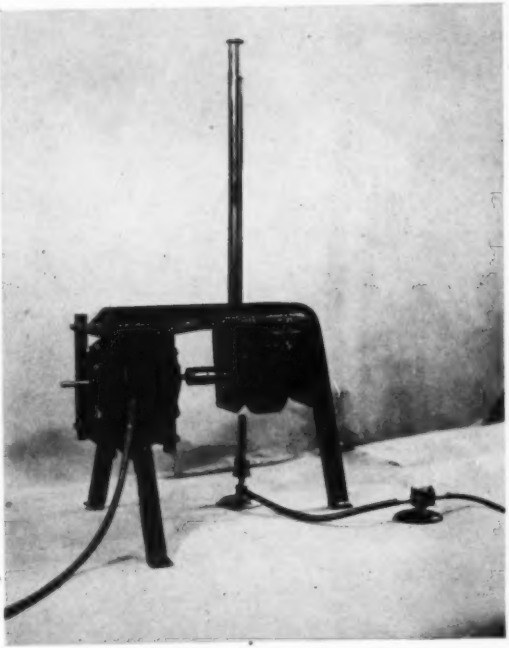

FIG. 1.

OXIDATION INSTRUMENT DESIGNED BY MOLLINGER.

[*To face p.* 72.

this is fitted to the upper part of the apparatus. Then the saw, driven by an electric motor at 2800 r.p.m., is made to rotate. As a result, the oil is flung in minute particles towards the chimney and flows back along the sides into the tank. At the same time the gas-burner under the tank is lit. As soon as the dispersed oil has attained the temperature of the test, this temperature is kept constant for 85 minutes, which is quite feasible up to 230° C. with a fluctuation of $\pm$ 1° C.

As is evident from Fig. 2, a certain amount of air, passing between the two loosely-fitted rings rotating with the axle and the sides of the tank, will reach the oil and promote oxidation. The oil fumes escape through the chimney, the upper part of which is provided with four slanting partitions. Oil fumes also escape through the small apertures between the rotating rings and the sides of the tank. The thermometer is placed almost immediately above the gas-burner, projecting 5·8 cm. into the tank. The velocity with which the oil moves at the bottom of the tank makes superheating impossible.

At the end of the ageing test a short interval is allowed for the oil to cool, if necessary, after which the tank with the oil is weighed to the nearest 0·5 gm. in order to determine the loss by evaporation. The aged oil is then further examined.

We have now aged seventy-eight different lubricating oils for diesel engines at 230° C. in the oxidizer described and illustrated here.

We preferred this high ageing temperature because we consider this to be right for diesel engines. This opinion is corroborated by Mr. Fairlie's citation [32] of 232–371° C. for piston temperatures, all according to the load.

As it has not yet been possible to put several of the above-mentioned seventy-eight lubricating oils through engine tests, we have to be very careful in interpreting the results of these ageing tests, and we must not attach a definite value to them as regards a quality test for service.

Although many indications have been provided, we do not yet wish to call them proofs.

Thus one of the two kinds of lubricating oil used in our diesel engines thickens more than the other; this agrees with the oxidation test. It is furthermore evident from the results of the oxidation tests with the seventy-eight lubricating oils that the pure Pennsylvania oils age least of all and are in this test superior to the naphthene base oils. This fact is borne out by several statements in the relevant literature ([21, 25, 27, 32, 39, 40]). It was also found that many solvent-treated oils age considerably. This finds corroboration in some publications and refutation in others ([11, 32, 34, 40]).

Besides the ageing test in our instrument, the Indiana oxidation test was also carried out with forty-one different oils in a co-operating laboratory.

Appraised and classified in the same way, both oxidation tests of twenty-seven kinds of oil correlate fairly well, whereas with the remaining fourteen oils the comparison turns out rather badly. This unfavourable result is not surprising, since the method of ageing is quite different.

In the literature the oxidation tests often tally well with the corresponding engine tests ([2, 5, 9, 13, 15, 30, 35]). On the other hand, however, several oxidation tests are mentioned which do not agree ([4, 17, 18]).

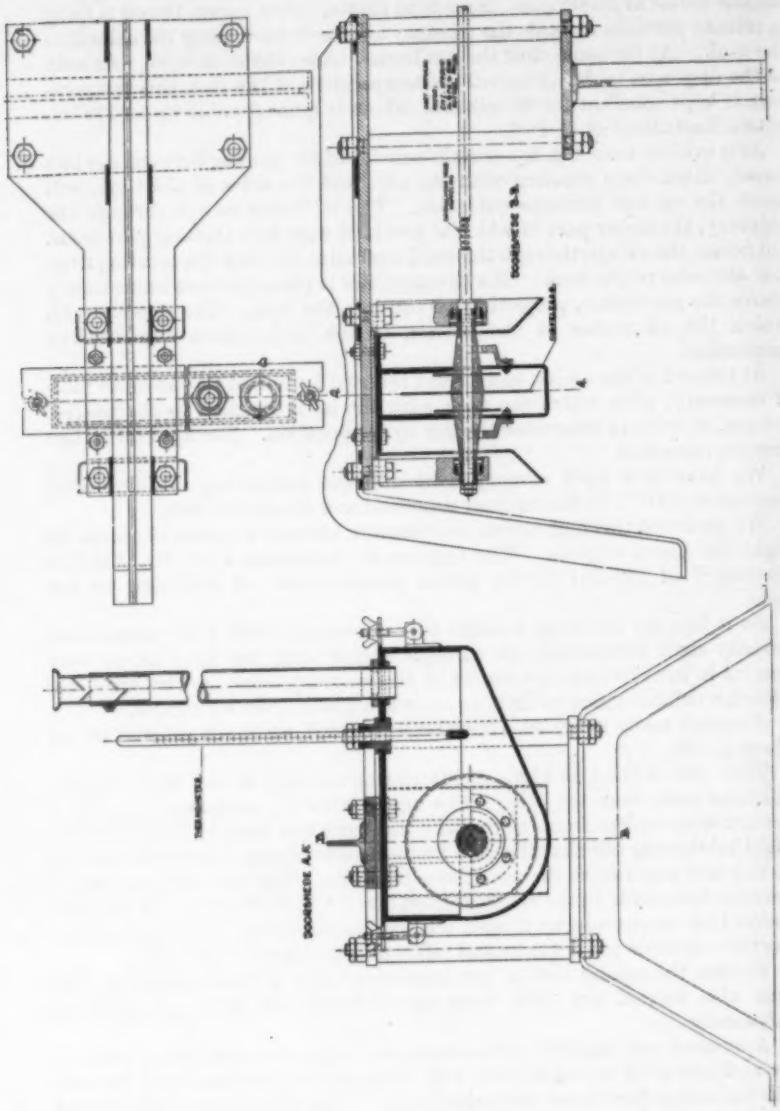

FIG. 2.
PLAN OF OXIDATION INSTRUMENT DESIGNED BY MOLLINGER.

The lubricating oil aged in the instrument is tested for :

(1) sludge (soluble in benzene);
(2) viscosity at 100° C. in centipoises;
(3) acid number;
(4) saponification number;
(5) Conradson residue.

Short Description of The Methods of Test.

(1) The sludge content is determined by adding 5 gm. of oil to 200 cu.cm. of petroleum ether (boiling range 40–60° C.). The liquid is kept for about 24 hours in a dark place, after which, by repeated centrifuging with petroleum ether, the sludge is weighed in the tube after drying for 1 hour at 105° C.

(2) The viscosity at 100° C. is determined by the Vogel–Ossag viscometer with an excess pressure of 60 cm. of water.

(3) For the acid number 100 cu. cm. of neutralized 96 per cent. alcohol is added to the weighed quantity of oil (about 4 gm.) in an Erlenmeyer flask. After boiling for a short time and cooling for 10 minutes, the solution is filtered. The filtrate is titrated with $\frac{1}{10}N$-KOH with phenolphthalein as indicator.

(4) For the saponification number 25 cu.cm. of alcoholic KOH are added to the weighed quantity of oil (about 2 gm.) in an Erlenmeyer flask. The mixture is then boiled for an hour, a long glass tube serving for cooler. It is then titrated with 0·5N-hydrochloric acid and phenolphthalein as indicator; after the turning-point to colourless is reached, it is boiled for a further 5 minutes and again titrated after more drops of the indicator have been added. A blank test is made at the same time.

The saponification number is :

$$\frac{\text{cu. cm. 0·5}N\text{-HCl for blank test} - \text{cu. cm. 0·5}N\text{-HCl for determination}}{\text{weighed quantity of oil}} \times 56{\cdot}16.$$

(5) The Conradson residue is determined by the prescribed method with the standard apparatus for the test.

In Table 1 are given the different metals with which the lubricating oil comes into contact in the Maybach diesel engines and their chemical composition.

Minute turnings of these twelve different metals were cut with a diamond-cutter. The catalytic effect of each of these metals on the ageing is determined by adding in each case 0·3 per cent. of the turnings, in order to age the lubricating oil in the above-mentioned oxidation instrument at 230° C. for 85 minutes.

Although not all the metals in the engine will come into contact with the lubricating oil at 230° C., the temperature is nevertheless kept the same in all the tests, in order at any rate to be able to make a comparison at 230° C.

It goes without saying that after each test the tank, the saw, etc., are thoroughly cleaned, so that not a single metal particle from the preceding test shall be left behind. All the tests were duplicated. Before analysing

FIG. 2.
PLAN OF OXIDATION INSTRUMENT DESIGNED BY MOLLINGER.

TABLE I.

	Cylinder cast iron *A*.	Cylinder cast iron *B*.	Cast iron of piston-rings.	Copper containing silumin of the pistons.	Copper containing silumin of the crank-case.	Chromium steel of roller main bearing.	Chromium nickel tungsten steel of roller connecting rod bearing.	Chromium nickel tungsten steel of ra.e connecting rod bearing.	Aluminium manganese bronze of cage connecting rod bearing.	Chromium nickel steel of pumping wheel.	Rod copper of tube oil filter.	Brass of wire cloth from oil filter.
Phosphorus, %	0·100	0·112	0·580	—	—	—	—	—	—	—	—	—
Sulphur, %	0·136	0·115	0·096	—	—	—	—	—	—	—	—	—
Manganese, %	0·84	0·84	0·63	0·46	0·16	0·30	0·41	0·36	3·3	—	—	—
Silicon, %	2·34	2·36	2·60	13·3	13·4	0·19	0·26	0·28	—	0·42	—	—
Total carbon, %	3·30	3·26	3·40	—	—	1·0	0·70	0·62	—	0·24	—	—
Graphite, %	2·62	2·56	2·91	—	—	—	—	—	—	0·34	—	—
Combined carbon, %	0·68	0·70	0·49	—	—	—	—	—	—	—	—	—
Chromium, %	—	—	—	—	—	1·4	1·14	1·3	—	0·66	—	—
Nickel, %	—	—	—	—	—	nil	4·35	4·1	—	3·28	—	—
Tungsten, %	—	—	—	—	—	traces	0·64	0·41	—	nil	—	—
Copper, %	—	—	—	1·40	1·0	—	—	—	88·2	—	rest	64·6
Zinc, %	—	—	—	—	—	—	—	—	traces	—	nil	35·2
Tin, %	—	—	—	—	—	—	—	—	traces	—	nil	nil
Lead, %	—	—	—	nil	nil	—	—	—	traces	—	nil	nil
Magnesium, %	—	—	—	0·52	0·11	—	—	—	—	—	—	—
Iron, %	—	—	—	3·50	0·96	—	—	—	0·4	—	nil	nil
Aluminium, %	—	—	—	rest	rest	—	—	—	8·2	—	nil	—
Arsenic, %	—	—	—	—	—	—	—	—	—	—	nil	—

the aged lubricating oil, the added minute metal turnings are removed by hot suction through a filter cup.

The lubricating oil used was a paraffin base oil, approximately meeting the specifications for lubricating oil *A*, mentioned later in this article.

In Table II are given the results of the ageing tests with the addition of 0·3 per cent. of minute metal turnings, tabulated according to the decreasing positive effect on the ageing, with regard to the viscosity. For purposes of comparison, this table also includes the results of tests made in this experiment with the non-aged and also with the aged lubricating oil without the addition of metal.

TABLE II.

Lubricating oil with addition of 0·3% very fine turnings of metals mentioned below.	Results of analysis after ageing at 230° C. for 85 minutes.					
	Loss by evaporation, %.	Sludge (soluble in benzene).	Acid number.	Viscosity at 100° C., c.p.	Conradson residue, %.	Saponification number.
Chromium nickel steel of impeller	23·0	12·7	4·25	354·9	9·12	56·2
Chromium nickel tungsten steel of roller connecting rod bearing	23·2	13·2	3·8	288·8	8·80	44·6
Chromium steel of roller main bearing	23·0	10·5	3·9	266·2	8·87	45·1
Cast iron of piston rings	21·5	9·2	3·5	262·7	8·62	45·1
Chromium nickel tungsten steel of race connecting rod	23·2	9·6	4·05	201·6	8·52	47·7
Cylinder cast iron *A*	22·7	9·0	4·0	189·3	8·59	40·7
" " *B*	22·7	8·1	4·0	176·3	8·14	40·5
Copper containing silumin of pistons	22·2	7·6	3·4	154·6	8·11	43·8
Copper containing silumin of the crank case	21·0	7·3	4·0	122·4	7·48	41·4
Brass of wire-cloth from oil filter	21·7	4·8	3·6	115·1	7·31	37·4
Red copper of tube oil filter	18·2	1·9	2·7	70·0	6·42	32·7
Aluminium manganese bronze of cage connecting rod bearing	18·5	0·95	2·6	53·3	5·32	29·5
Lubricating oil *without* addition of metal	22·0	7·5	3·5	148·1	8·13	45·8
Original lubricating oil non-aged	—	nil	0·15	15·7	0·89	nil

The following is evident from Table II.

(1) All the ferrous metals more or less increase the ageing of the lubricating oil. The non-ferrous metals have no effect at all, or a negative catalytic effect.

(2) On the whole the alloyed steels increase the ageing more than the two kinds of cast iron. The chromium-nickel tungsten steel of the race of the connecting-rod bearing is the only exception to this, but it is only manifested in the values for viscosity and Conradson residue.

(3) It is quite possible that the strongly positive catalytic effect on the ageing of the chromium nickel steel of the impeller may be caused by the absence of tungsten and the low content of carbon and chromium.

(4) The cylinder-cast irons *A* and *B* have practically the same effect on the ageing, which agrees with the identity of chemical composition.

The cast iron of the piston rings increases the ageing of the lubricating oil more than does the cylinder-cast iron.

The much higher content of phosphorus may account for this.

(5) Of the non-ferrous metals the copper-containing silumin of the pistons has only a very slight effect on the ageing. The negative catalytic effect begins with the copper-containing silumin of the crank-case.

A striking effect is the pronounced counteracting effect on the ageing of the copper of the tube oil-filter, and especially of the aluminium-manganese-bronze of the cage connecting rod-bearing.

(6) On the whole there is some connection between the alterations in viscosity and those of the sludge content and the Conradson residue. The saponification and acid numbers do not form a steadily decreasing series and have little connection with each other. The loss by evaporation is scarcely affected by the addition of metals. It is only with copper and aluminium manganese-bronze, which counteract the ageing considerably, that there is less loss by evaporation.

The question raised at the beginning of this paper, viz., whether the metal splinters present in the used lubricating oil and also the cylinder wall, piston-ring, piston, etc., will change the content of oxidation products, may be answered in the affirmative.

As a matter of course, it is mainly the iron metals which will come into contact with the lubricating oil in the engine. The catalytic effect of these metals is doubtless positive; consequently the lubricating oil will age more and the oxidation products will increase.

As has been previously mentioned, a striking fact is the strong inhibiting effect copper has upon the ageing of the lubricating oil at 230° C. It is, however, known that copper is deleterious [43]; *e.g.*, this is the case with transformer and turbine oils.

The temperature to which transformer oil especially is exposed, being much lower than 230° C., we have extended the test with copper in order to determine the catalytic effect of an addition of 0·3 per cent. of minute turnings on the ageing at rising temperature, viz. at 100° C., 140° C., 180° C., 183° C., 187° C., 193° C., 205° C., 218° C., 224° C. and 230° C.

In order to ascertain whether the catalytic effect of copper is the same on the ageing of different kinds of lubricating oils, we carried out the same experiment with a naphthene base oil. The above-mentioned temperatures have been purposely chosen, because the series of tests with the paraffin-base oil required this, as will be evident below.

The specifications of the two lubricating oils under test are tabulated below.

Determinations.	Lubricating oil *A* on paraffin base.	Lubricating oil *B* on naphthene base.
Specific gravity at 15° C.	0·886	0·912
Flash point (open cup)	243° C.	223° C.
Fire point (open cup)	292° C.	274° C.
Viscosity at 20° C.	654·9 c.p. = 97·7° E.	655·5 c.p. = 95° E.
,, 50° C.	91·1 ,, = 15·2° E.	79·7 ,, = 11·8° E.
,, 100° C.	14·5 ,, = 2·61° E.	10·7 ,, = 2·08° E.
Hard asphalt	nil	nil
Soft asphalt + paraffin wax	,,	,,
Foreign matter	,,	,,
Loss of weight on heating to 150° C.	0·03%	0·04%
Pour point (Neth. Railways method)	−17° C.	−19° C.
Acid number	0·17	0·26
Conradson residue	0·89%	0·41%
Sulphur	0·20%	0·87%
Aniline point	117·8° C.	92·0° C.

The tests were all carried out in duplicate, the first series, from 100° C. to 230° C., being finished off first and then the second. Between the two series the instrument was thoroughly cleaned.

In each case the specific gravity at 15° C., the sludge content (soluble in benzene), the viscosity at 100° C. in c.p., the Conradson residue, the acid number and the saponification number of the aged lubricating oil were determined.

The methods of test have already been described in this paper. The specific gravity is determined with a pyknometer.

Of the whole process of each of the six determinations a graph has been made showing the changes owing to the ageing at rising temperature of the lubricating oil without and with the addition of 0·3 per cent. of minute copper turnings.

The research results with lubricating oil *A* are represented in Figs. 3, 4, 5, 6, 7 and 8.

From these graphs it is evident first of all that the catalytic effect of the added copper on the ageing of the lubricating oil at lower temperatures is quite different from that at higher temperatures. Apart from the sludge which begins to form above 218° C. in the lubricating oil (without copper) in the case of the five remaining determinations, the catalytic effect of copper at 180° C. changes from clearly but weakly positive to strongly negative. This result removes the contradiction noted with copper (see Table II). The above-mentioned results accord more or less with the statements of A. Maillard [8] and M. Moutte, Dixmier and Lion.[16]

It is evident from the shape of the graphs that Fig. 4 (sludge) and Fig. 5 (viscosity) are closely connected, which is also the case with Fig 3 (specific gravity), Fig. 6 (Conradson residue), Fig. 7 (acid number) and Fig. 8 (saponification number).

The two first-mentioned graphs show that above 218° C. the viscosity of the oil without copper is raised considerably, owing to a rapidly increasing sludge content.

As the copper represses the formation of sludge very considerably, the negative catalytic effect on the viscosity is most clearly shown at 230° C.

The course of the viscosity is, moreover, affected by the loss by evaporation, which increases gradually up to 5 per cent. as far as 205° C. for the oil without copper and then jumps suddenly at 218° C., 224° C. and 230° C. to 15·5 per cent., 16 per cent. and 21·5 per cent.

Up to 205° C. copper does not show any effect, whereas at 218° C., 224° C. and 230° C. the loss by evaporation falls to 9·5 per cent., 14 per cent. and 18·5 per cent.

As regards the other four determinations, the negative catalytic effect of copper increases from 180° C. to 218° C. rather quickly on the whole. Above 218° C. the anti-oxidizing effect of copper rapidly decreases.

The connection between the acid number and the saponification number, moreover, stands out clearly in Figs. 7 and 8.

The sharp fall in the acid number between 180° C. and 183° C. is worthy of note. The specific gravity likewise substantially decreases (Fig. 3).

It may finally be inferred from the fact of the similarity between the shapes of the graphs of the specific gravity and the Conradson residue (respectively Fig. 3 and Fig. 4) that a connection exists between the two

determinations. This connection emerges equally clearly from the oil with or without the addition of copper.

Below we give the results of the tests obtained on lubricating oil B, represented in Figs. 9, 10, 11, 12, 13 and 14.

In absolute contrast to lubricating oil *A*, copper in lubricating oil *B* has only a slight catalytic effect on the ageing. With all the graphs the dotted line runs closely along the drawn line, or winds round it several times. Only in Fig. 10 (sludge) does a turning-point become clearly visible at approximately 197° C. However, the change here is from negative to positive, although the catalytic effect of copper is slight, below as well as above 197° C.

With this lubricating oil there is no similarity between the viscosity and sludge curves (Fig. 11 and Fig. 10).

The pronounced increase in the sludge content, beginning at 205° C. does not entail considerably increased viscosity, although the loss by evaporation at the higher temperatures increases a good deal more than with lubricating oil *A*.

Accordingly Figs. 13 and 14 show much less similarity than Figs. 7 and 8 with lubricating oil *A*.

The only analogy to lubricating oil *A* is the similar shape of the curves of the specific gravity (Fig. 9) and the Conradson residue (Fig. 12).

Here again, then, is found some connection between the course of these two determinations.

Needless to say, copper also only very slightly affects the loss by evaporation.

The two above-mentioned tests prove convincingly that the catalytic effect of copper may be practically nil, but also weakly positive as well as very strongly negative, all according to the kind of lubricating oil used and to the ageing temperature. The fact that the catalytic effect on the ageing depends very much on the kind of lubricating oil used has been previously noticed by E. W. J. Mardles.[21]

Finally, let us try to realize what reactions come into play while the two lubricating oils *A* and *B* are ageing in the oxidation apparatus designed by A. Mollinger.

It is stated in the literature ([1, 4, 6, 9, 10, 11, 12, 16, 19, 20, 21, 23, 24, 25, 31]) that the following reactions may occur during the ageing of lubricating oil :

(1) Oxidation involving primarily the formation of acids, and secondarily what are known as petroleum resins, etc., proceeding by condensation from these acids.

At higher temperatures asphaltic matter originates, formed entirely or in part at the expense of the acids and the petroleum resins. This asphaltic matter is completely or partly soluble in the lubricating oil.

(2) Condensation or polymerization. Although there is a difference of opinion as to which of these two reactions takes place, we shall speak about condensation.

Explanation of Figs. 3–8.

———— = Lubricating oil A without addition.
– – – – – – – – = Lubricating oil A with 0·3% of very fine copper turnings.
⊙ = Lubricating oil A original before ageing.

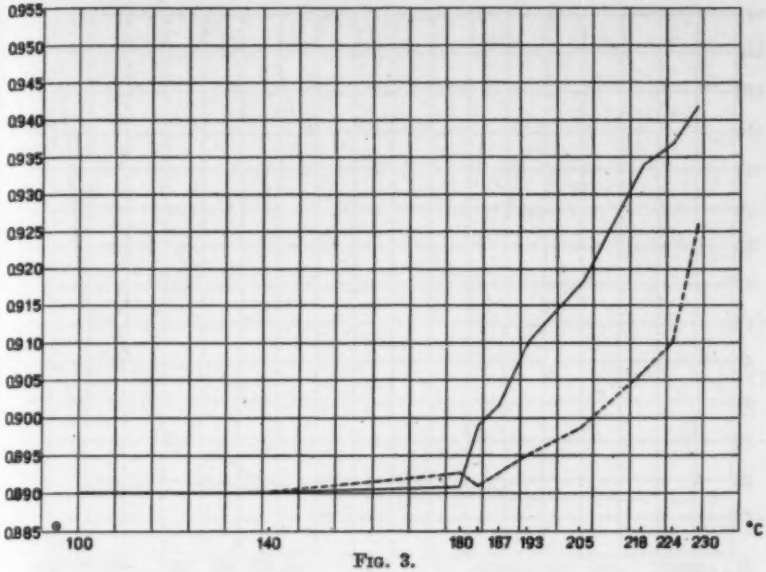

FIG. 3.

CHANGE IN SPECIFIC GRAVITY AFTER AGEING AT DIFFERENT TEMPERATURES.

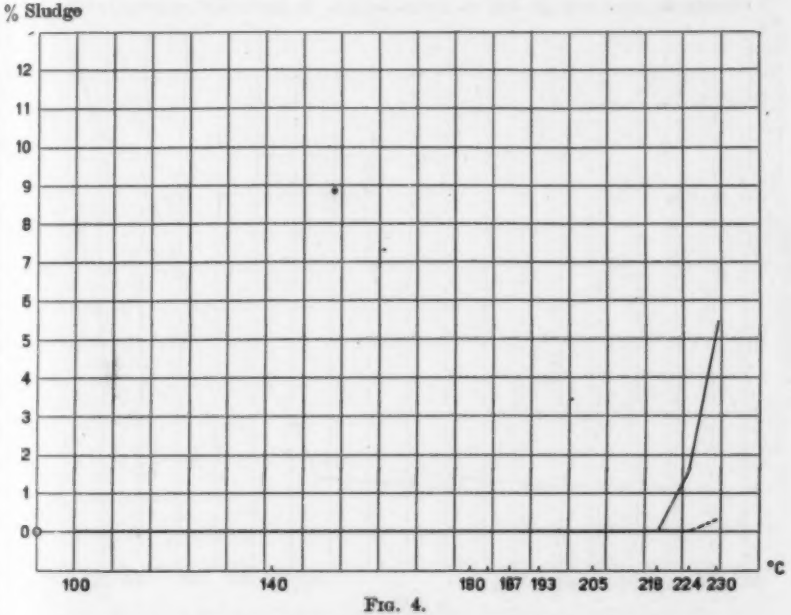

FIG. 4.

FORMATION OF SLUDGE (SOLUBLE IN BENZENE) AFTER AGEING AT DIFFERENT TEMPERATURES.

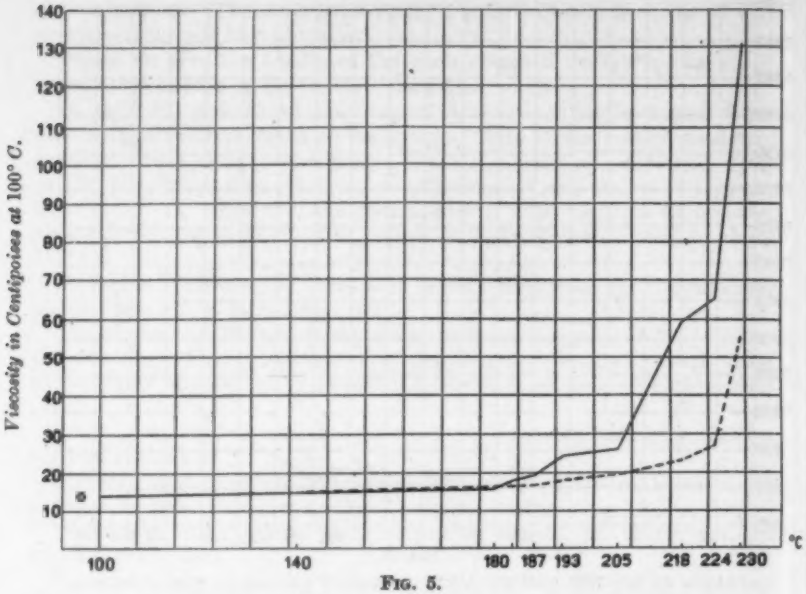

FIG. 5.

CHANGE IN VISCOSITY AT 100° C. AFTER AGEING AT DIFFERENT TEMPERATURES.

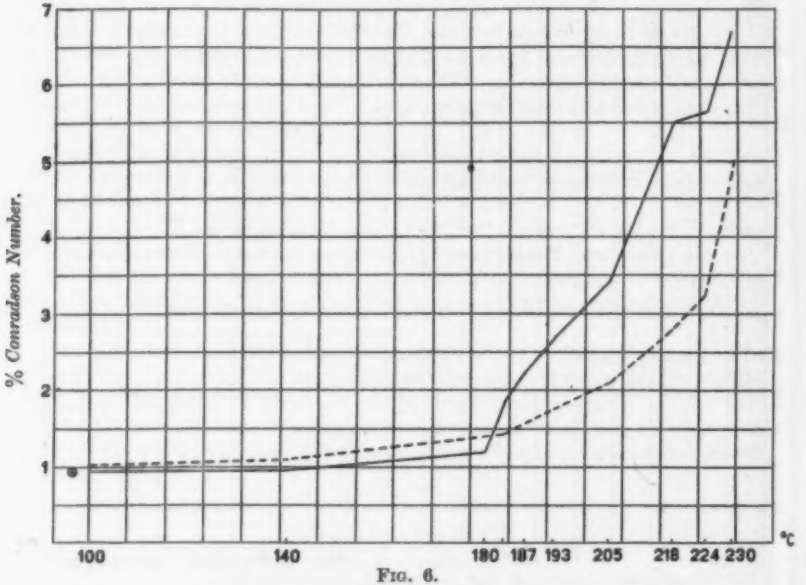

FIG. 6.

CHANGE IN CONRADSON CARBON RESIDUE AFTER AGEING AT DIFFERENT TEMPERATURES.

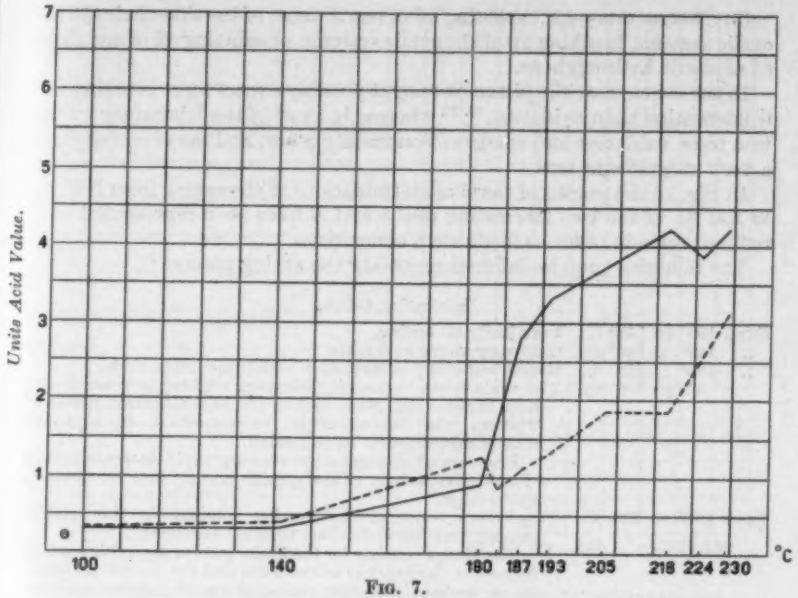

FIG. 7.

CHANGE IN ACID VALUE AFTER AGEING AT DIFFERENT TEMPERATURES.

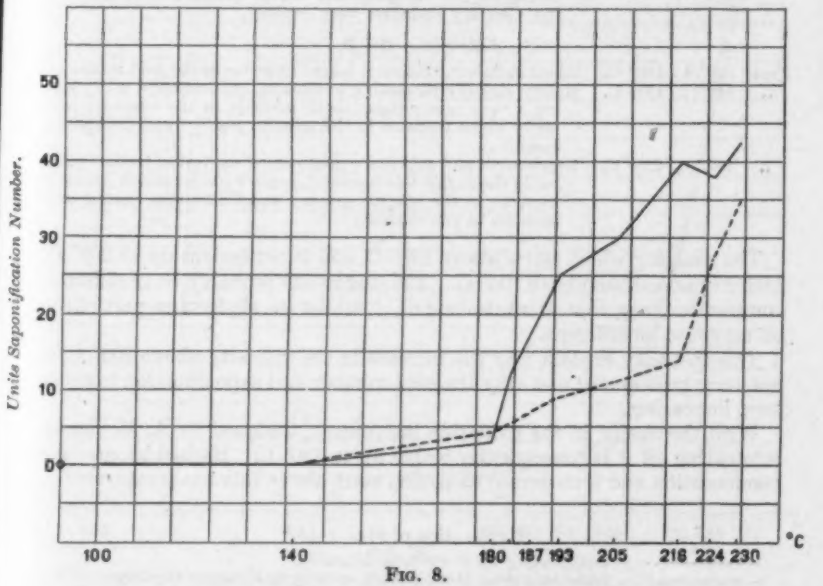

FIG. 8.

CHANGE IN SAPONIFICATION NUMBER AFTER AGEING AT DIFFERENT TEMPERATURES.

(3) Destruction—*i.e.*,, splitting off of one or more of the side-chains of the cyclic systems, breaking up of the cyclic systems, or splitting off of one chain of aliphatic hydrocarbons.

In the engine near the piston one might possibly expect more cracking and condensation than oxidation,[19, 23] whereas in most of the laboratory oxidation tests, oxidation and condensation mainly occur, and the cracking plays a very insignificant part.

In Fig. 15 the graphs of the six determinations of the ageing from 100° up to 230° C. of the two lubricating oils *A* and *B* have been represented on a reduced scale in order to facilitate a comparison.

The following may be inferred regarding the ageing process:

Lubricating Oil A.

From 100° to 140° C.	Practically no ageing.
„ 140° „ 180° C.	Only very slight oxidation.
„ 180° „ 218° C.	Rapid beginning of oxidation which generates acids.
Above 193° C.	The acids begin to resinify (showing slighter increase in the acid number and rapid rise in the saponification number) whereas the conversion to, or formation of asphaltic matter may already have started. Pronounced condensation causing rapid increase in the viscosity, especially of the specific gravity and the Conradson residue.
From 218° to 230° C.	Progressive condensation (further increase in the specific gravity and the Conradson residue) (sludging). The sludge consists for the major part of asphaltic matter, formed at the expense of the acids and the petroleum resins in particular. For this reason the acid number and the saponification number above 218° C. change only a little. Owing to the sludging and the progressive condensation, the viscosity increases very rapidly.

Lubricating Oil B.

From 100° to 140° C.	Minor incipient oxidation (slight increase in the acid number).
„ 140° „ 193° C.	Mainly steadily increasing oxidation, condensation still playing a very minor part (slight increase in the viscosity and fairly slight increase in the specific gravity and Conradson residue).
„ 193° „ 230° C.	Progressive and still more pronounced oxidation (rather more rapid rise in the acid number), greater condensation (marked increase in the specific gravity and Conradson residue and increase in the viscosity).

The sludging which starts above 180° C. and is not serious up to 205° C. gathers momentum above 205° C. The sludge will probably be of different composition from that of lubricating oil *A*, whilst the sludge-free part of the oil may also be different.

This fact may explain why the increase in the viscosity above 205° C. is not very pronounced and why the acid number and saponification number keep increasing.

With the ageing in the oxidation instrument, designed by A. Mollinger, lubricating oil *A* is consequently stable up to 180° C. Marked progressive condensation and a moderate oxidation start above this temperature.

Explanation of Figs. 9–14.

———— = Lubricating oil B without addition.
– – – – – = Lubricating oil B with 0·3% of very fine copper turnings.
⊙ = Lubricating oil B original before ageing.

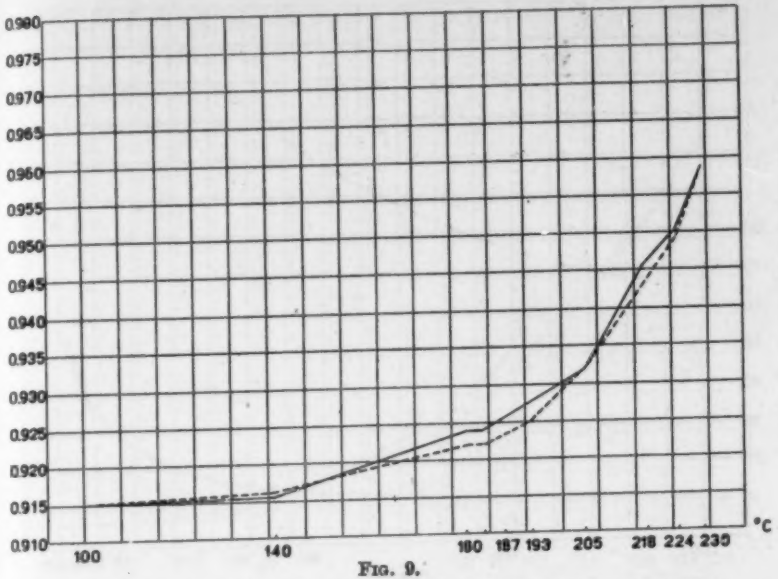

FIG. 9.

CHANGE IN SPECIFIC GRAVITY AFTER AGEING AT DIFFERENT TEMPERATURES.

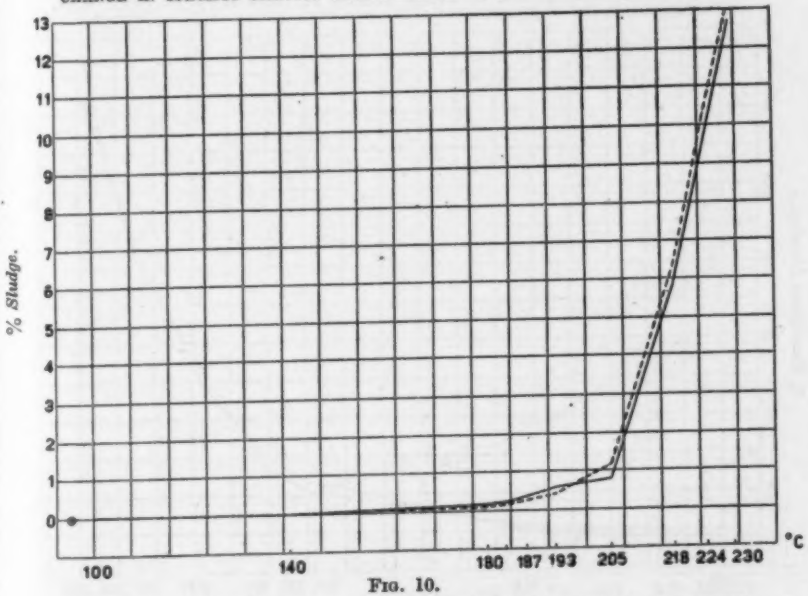

FIG. 10.

FORMATION OF SLUDGE (SOLUBLE IN BENZENE) AFTER AGEING AT DIFFERENT TEMPERATURES.

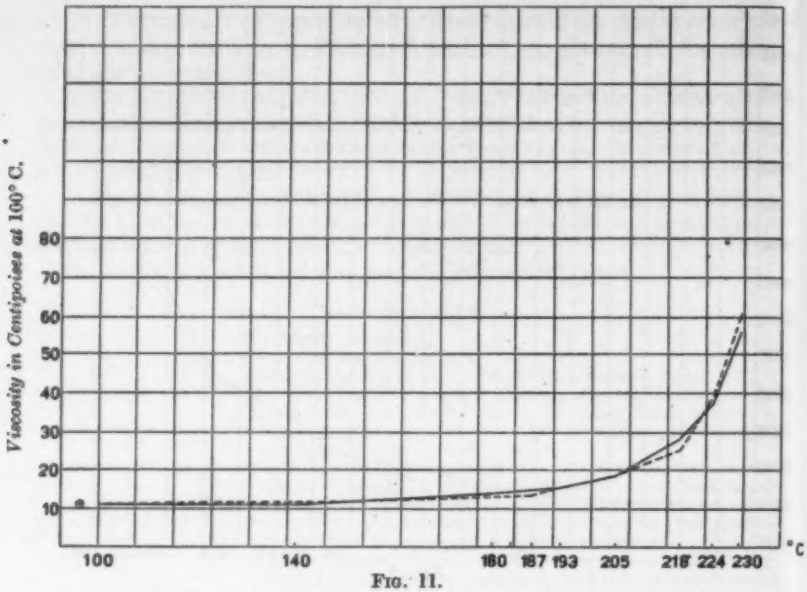

FIG. 11.

CHANGE IN VISCOSITY AT 100° C. AFTER AGEING AT DIFFERENT TEMPERATURES.

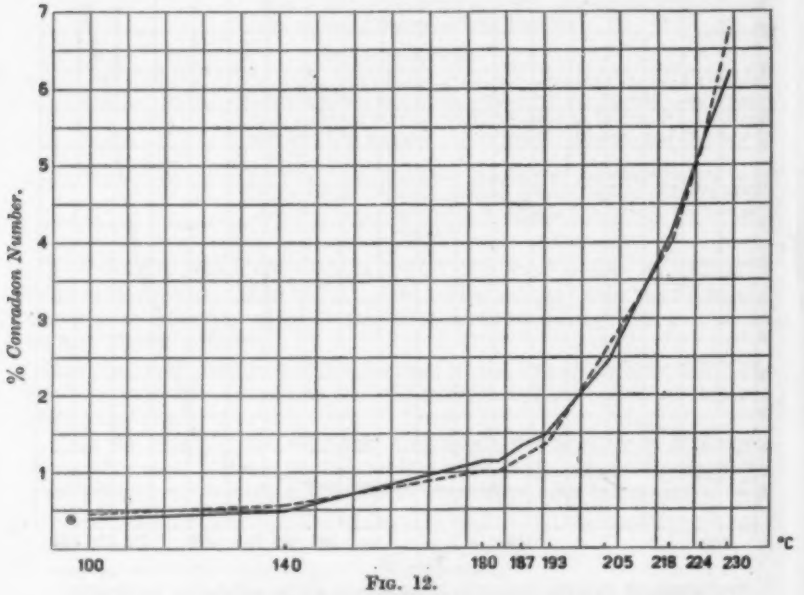

FIG. 12.

CHANGE IN CONRADSON CARBON RESIDUE AFTER AGEING AT DIFFERENT TEMPERATURES.

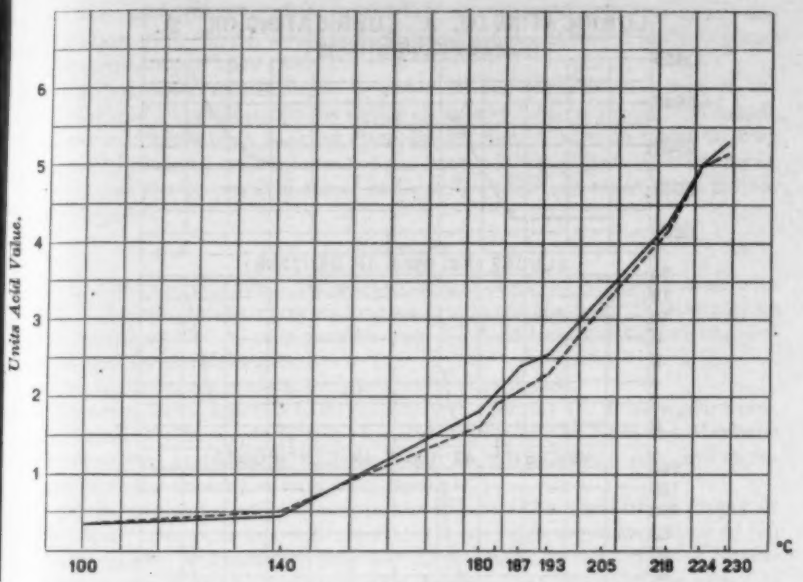

FIG. 13.

CHANGE IN ACID VALUE AFTER AGEING AT DIFFERENT TEMPERATURES.

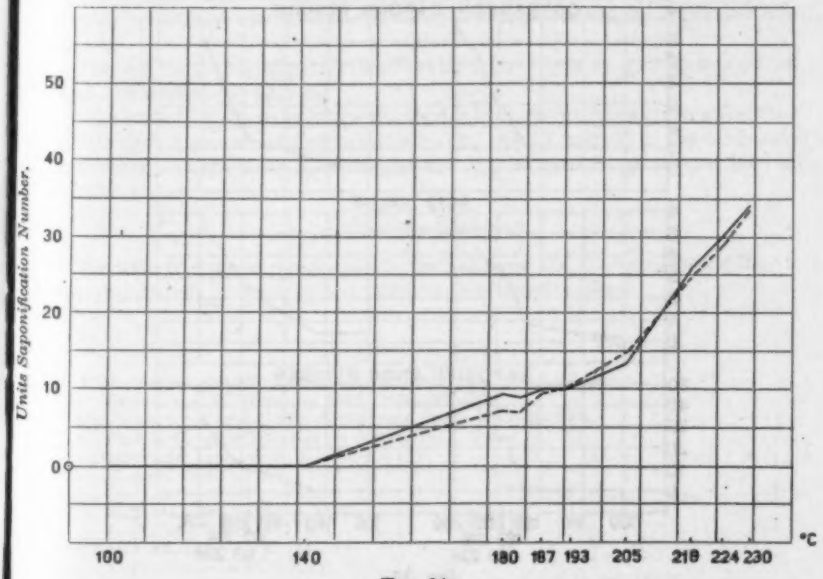

FIG. 14.

CHANGE IN SAPONIFICATION NUMBER AFTER AGEING AT DIFFERENT TEMPERATURES.

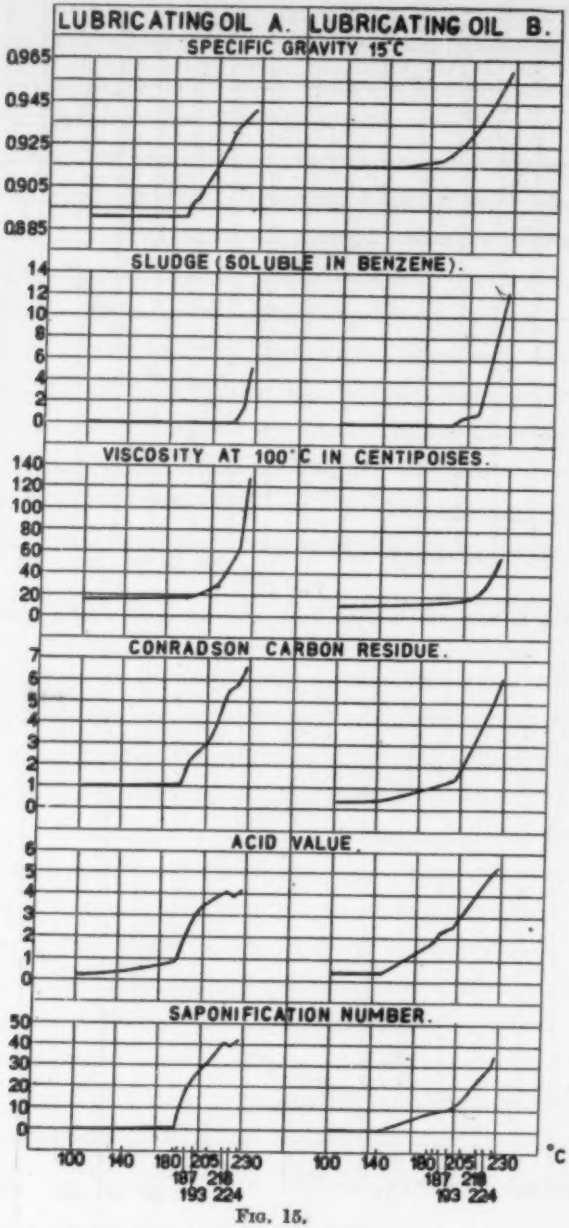

FIG. 15.

AFTER AGEING AT DIFFERENT TEMPERATURES.

Lubricating oil *B* is stable up to 140° C. Beyond this ever-increasing oxidation sets in, as does condensation, which, however, only becomes more pronounced above 193° C.

Further observations might be made on the remarkable course of the catalytic effect of copper on the ageing of the two lubricating oils. We shall, however, refrain from making them, as we should have to resort to very vague hypotheses, which have not yet been confirmed by any experiment. Nevertheless this problem seems to us sufficiently important to be further investigated.

Summary.

(1) The catalytic effect has been examined of all the relevant metals with which the lubricating oil comes into contact in the Maybach diesel engine on the ageing at 230° C. of a paraffin base oil *A*, in the oxidation instrument designed by A. Mollinger.

All the ferrous metals stimulate ageing more or less.

The non-ferrous metals have no catalytic effect at all, or a negative one.

The minute iron splinters in the used lubricating oil from the Maybach diesel engine, and also the cylinder wall, piston-ring, piston, etc., will therefore alter the content of oxidation products.

(2) From the investigations into the effect of the addition of copper as very fine turnings to a paraffin base oil (*A*) and to a naphthene base oil (*B*) during ageing progressively from 100° C. to 230° C. in the oxidation instrument designed by A. Mollinger, it is evident that the catalytic effect of copper is very different in the case of the two lubricating oils.

With the paraffin base oil the catalytic effect up to 180° C. is clearly but weakly positive, whereas above 180° C. copper strongly represses the ageing.

There is only a slight catalytic effect over the whole range of temperature with the naphthene base oil.

(3) Guided by the data of the relevant literature, we have given an outline of the ageing process of the two lubricating oils (*A* and *B*) in the oxidation instrument designed by A. Mollinger at temperatures ranging from 100° C. to 230° C.

Acknowledgement.

We wish to express our thanks to the analysts, Mr. R. Monster and Mr. J. van den Brink, for making the tests for this investigation.

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BURNING TEST FOR KEROSINE.*

I.P.T. Serial Designation—K 35 (T).

Apparatus.

The lamp to be used for this test shall consist of an oil chamber, a burner, and a chimney conforming substantially to the dimensions stated in Fig. 1.†

It is essential to ensure that the burner fits vertically into the lamp reservoir, and that the wick guide has parallel sides and is centrally disposed in relation to the slot in the dome of the burner. Any distortion of the wick guide and/or dome will make the production of the necessary flame shape difficult and render subsequent char values unreliable.

Wick.—The wick shall be a ¾-in. (1·9-cm.) paraffin flat wick, super quality, as manufactured by Messrs. Morgan, Crossley & Co., Ltd.‡ It shall contain approximately 43 ends of 3-ply yarn, woven double plain weave with stitching ends, one blue stripe on one face and one green stripe on the reverse face: woven with approximately 15 picks per inch and weighing normally ½ oz. per yard.

After weaving the wick shall be purified by boiling in distilled water and thoroughly dried.

After drying, the wick shall be made into rolls and left for 7 days before finally cutting into 8-inch (20·3-cm.) lengths. After cutting, the wick shall be packed into metal (tin) containers.

The maximum ash content of the wick shall be 0·4%.

Preparation of Apparatus.—New lamp glasses shall be soaked in diluted hydrochloric acid (1 : 1) for 24 hours, cleaned with a test-tube brush, and rinsed thoroughly with distilled water. The glasses shall then be subjected to three preliminary 24-hour burning periods before being used for burning tests.

After use, glasses shall be thoroughly cleaned, rinsed with distilled water and dried. Prior to each test the burner shall be thoroughly cleaned, removing any deposit from the wick guide, air holes and ducts. The oil container shall also be rinsed two or three times with a little of the oil to be tested. For each test a new piece of wick shall be dried in a steam oven for thirty minutes, soaked in the oil while still hot and fitted into the wick guide. The length of wick used shall be 8 in. (20·3 cm.).

The test shall be made in a well-ventilated room free from draughts.§

The minimum temperature of the room and the oil in the container at the start and during the test shall be 60° F. (15·5° C.). Lamps shall be so

---

* This method supersedes the method issued in 1938.

† Suitable lamps, burners and chimney glasses can be obtained from the Lamp Manufacturing and Railway Supplies, Ltd., River Plate House, 12/13, South Place, E.C.2, but they should be checked as regards dimensions before being used.

‡ Messrs. Morgan, Crossley & Co., Ltd., Ducie Mills, Manchester, 10.

§ If necessary, a suitable screen about 2 ft. (60 cm.) diameter should surround the lamp to ensure this.

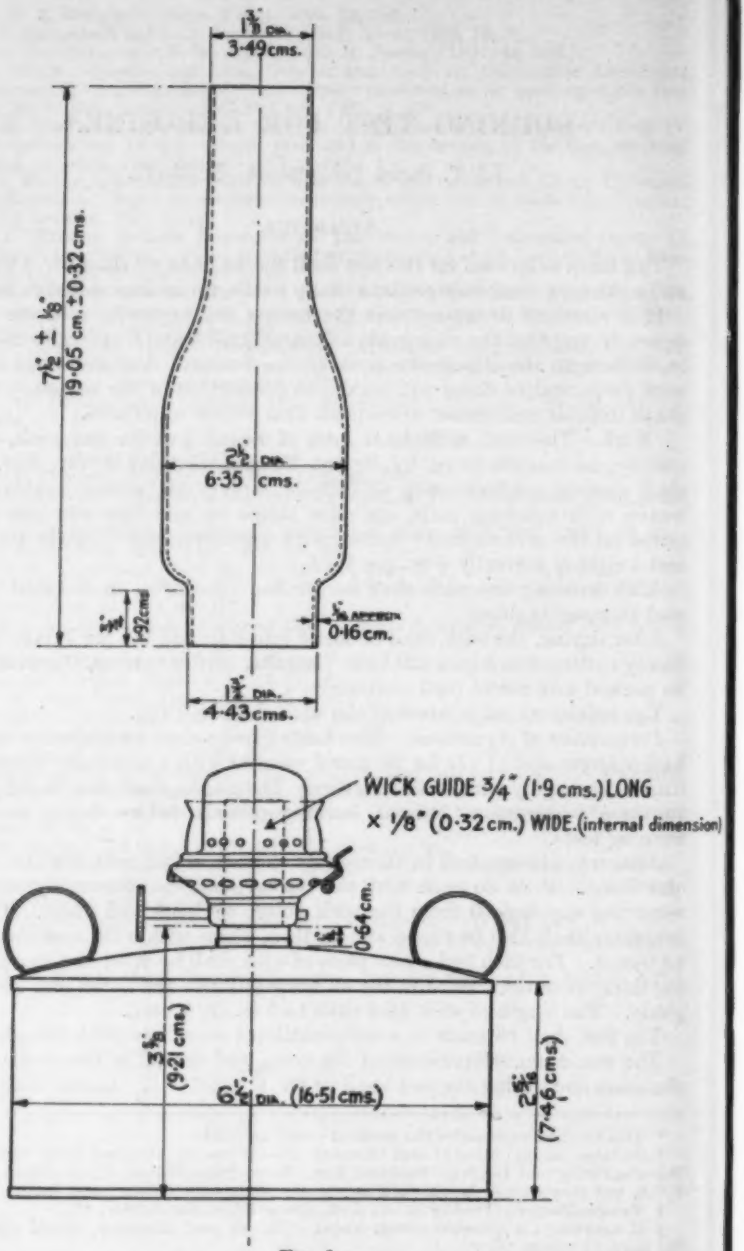

FIG. 1.

Note.—The tolerance on the chimney dimensions shall be ± 1/64" except where otherwise stated.

placed as to be at least 1 ft. (30 cm.) apart and 1 ft. (30 cm.) from any wall.

Duration of Test.

The test shall normally be of 24 hours duration, but in cases of dispute the duration of the test shall be 48 hours.

Method.

900 mls. of the oil shall be placed in the container,* and the burner, with the wick and clean chimney, fitted to the lamp. The dome (with chimney attached) shall then be folded back, and the wick carefully trimmed with sharp scissors to produce a flame 1 in. (2·5 cm.) high (measured from the top of the dome) and 1 in. (2·5 cm.) in width. The flame shall be smooth and symmetrical. Diagram A, Fig. 2, illustrates the flame shape with essential dimensions. It is to be emphasized that flame shape has a strong influence on char formation, and that it is therefore necessary to produce a flame similar, as nearly as possible, to that illustrated. The operation of wick trimming shall be carried out as follows :—

(*a*) The wick to be cut level with the wick guide.

(*b*) An inch or two (2·5 to 5·0 cm.) of the wick to be exposed and, starting at a point approximately $\frac{1}{8}$ in. (0·3 cm.) from each corner, a triangular portion to be cut off, as illustrated in Diagram B, Fig. 2.

(*c*) The sharp corners produced by operation (*b*) to be very slightly rounded off.

(*d*) Ragged projections, if any, to be removed by slightly bevelling the top edges of the wick illustrated in Diagram C, Fig. 2.

After trimming the top of the wick, it shall be re-saturated with kerosine before proceeding with the test. The lamp shall be weighed and the flame adjusted to within $\frac{1}{16}$ in. (0·15 cm.) of the standard flame dimensions.

The measurements of the correct height and width may be obtained by the use of the "Rather" Burning Test Gauge (see A.S.T.M. Serial Designation D-187/30), but other gauges, capable of measuring vertical and horizontal dimensions within the accuracy specified, are equally suitable. The gauge shall be placed as near as possible to the flame (say, 6 in. (15 cm.) from it) during this operation.

The lamp shall be allowed to burn for one hour, and the flame shall then be re-adjusted, if necessary, to the standard height. No further adjustments shall be made throughout the test.

Burning shall now be continued for a further 23 hours, and at the end of this period the lamp shall again be weighed.

In the case of the 48-hour test the lamp shall then be recharged with sufficient kerosine to restore the original weight, and burning shall be continued for a further period of 24 hours. At the completion of the test the lamp shall be again weighed.

The total consumption and average consumption per hour shall be

* If the previous examination of the sample had indicated the presence of suspended matter, the oil shall be filtered through a No. 4 Whatman (or equivalent) filter paper before carrying out the burning test.

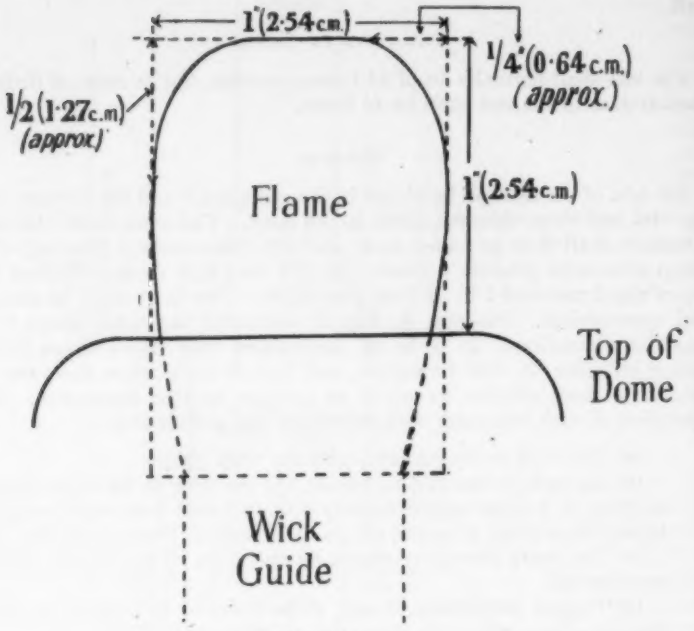

DIAGRAM A

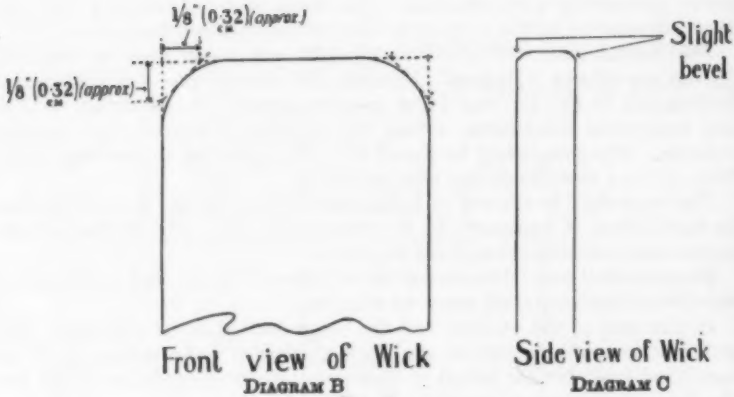

DIAGRAM B DIAGRAM C

FIG. 2.

recorded. (The average consumption will normally be approximately 20 grams per hour.)

Removal of Char.—A length of approximately ½ in. (1·3 cm.) from the charred end of the wick shall be cut off and placed, with any pieces of char which have been detached during burning, or adhere to the wick guide (the char being removed by gentle scraping with metal forceps), in a small beaker and well washed by decantation with petroleum ether. The beaker and contents shall then be dried at 105/110° C. for half an hour. After drying, the char shall be removed from the wick by—

(*a*) Breaking its structure by gentle pressure with metal forceps or similar instrument.

(*b*) Gentle scraping along and across the wick with the point of metal forceps or similar instrument.

Care shall be taken to ensure complete removal of char from the wick.

The mixture of char and fibre shall then be transferred to a glass plate or a sheet of glazed paper, pieces of thread from the wick shall be first removed, and the coarse char collected on a tared watch-glass. The fine, fluffy fibre shall then be removed as completely as possible from the mixture of fine char and fibre by tapping the mixture from one smooth surface to another, and gently brushing the mixture with a brush having short, stiff bristles. The object of brushing is to collect the fine fibre on the brush without removing the char. The mixture of fine char and fibre remaining on the glass or paper shall be finally brushed on to the watch-glass containing the coarse char, and the whole weighed. Results shall be expressed in milligrams of char per kilogram of kerosine, and duplicate results should be within the limits of $\pm$ 15% or $\pm$ 2 milligrams, whichever of these is the larger.

Recording of Results.

The following shall be recorded :

Total consumption in grams.
Average consumption per hour in grams.
Weight of dry char per kilogram in mgms.
Bloom on glass :

(*a*) Predominating colour : Brown, greyish-brown or grey.
(*b*) General remarks : Normal *or* Unsatisfactory.

The maximum and minimum temperatures of the test room shall be recorded, and any abnormal atmospheric conditions noted.

THE INSTITUTE OF PETROLEUM.

LUNCHEON.

FRIDAY, 26TH JANUARY, 1940.

A LUNCHEON of the Institute of Petroleum was held on Friday, 26th January, 1940, at the rooms of the Royal Empire Society, Northumberland Avenue, London, W.C. 2 (by courtesy of the Council of the Society). This Luncheon was held in lieu of the Annual Dinner of the Institute, cancelled in December 1939.

The President (Professor A. W. NASH) presided, and among those who were present were :

The Rt. Hon. Lord Cadman, G.C.M.G., D.Sc., Colonel L. Pineau (Chairman, The Anglo-French Executive Committee for Oil), Sir Cecil Kisch, K.C.I.E., C.B. (Vice-Chairman, The Anglo-French Executive Committee for Oil), the Rt. Hon. Sir Ronald Graham, P.C., G.C.B., Sir Andrew Agnew, G.C.B. (Chairman, The Petroleum Board), Monsieur J. Filhol, Messieurs J. E. Bouchandhomme, M. E. Goldet, Maurice Mercier, Mr. K. L. Stock, Mr. E. E. Soubry, Mr. R. W. Sellers, Lt.-Col. S. J. M. Auld, M.C., O.B.E., Professor J. S. S. Brame, C.B.E., Mr. T. Dewhurst, Dr. A. E. Dunstan, Mr. J. Kewley, Dr. A. J. V. Underwood and Mr. F. A. Yearsley.

After the loyal toast had been honoured, Sir Andrew Agnew, G.C.B., proposed the Toast of

"THE PERMANENT ANGLO-FRENCH EXECUTIVE COMMITTEE FOR OIL"

He said : The great privilege has fallen to me of proposing the toast of the Anglo-French Petroleum Executive Committee. I took the trouble this morning to find out whether that was the proper name for that body, and I found that it was not. (*Laughter.*) The proper name, I understand, is "The Permanent Anglo-French Executive Committee for Oil." I think that the two things have much the same meaning, and I am sure you will all agree with me that they mean something very big indeed, something which the ordinary man in the street may not realize is a task of tremendous magnitude. It is a task of absolutely the foremost importance at a time like the present, when our minds, both in France and throughout the British Empire, are centred on one thing and one thing only, and that is this war and the winning of it. Petroleum is going to be one of the winning factors in this war, and the body that is going to be mainly concerned with that winning factor is this body whose toast I am now proposing.

Who are the people who are concerned with this body ? First of all, we have with us to-day, I am glad to say, the Chairman of the Committee, Colonel Pineau. (*Applause.*) We have with us also the Vice-Chairman, Sir Cecil Kisch. (*Applause.*) We have also with us M. Filhol and Sir Ronald Graham, but I am sorry to say that, owing to his indisposition, we have not with us Mr. Starling. They are the five—the Big Five—who are the members of this Committee.

It is almost unnecessary, perhaps, for me to say very much about Colonel Pineau. We ought to realize that Colonel Pineau, after his distinguished war service, has controlled the petroleum affairs of France since the last war, and I can assure you that all the energy, the drive, the knowledge, and the experience that he had at that time are still with him. He has not lost one single little bit of his energy; he has not lost one single little bit of his power of perception; and I know perfectly well that once again he is going to be one of the main factors in winning this war. (*Applause.*)

LUNCHEON OF THE INSTITUTE OF PETROLEUM

London, 26th January, 1940.

[*To face p.* 96.

The Vice-Chairman is Sir Cecil Kisch, a name which is perhaps not very familiar to some of you in connection with petroleum affairs; he has come comparatively recently within the scope of the trade. I am going very briefly to tell you something about him. He is a man to watch. He has brought into this business an amount of energy and drive and an amount of common sense that I can assure you are above the average, no matter where you go; so keep your eye on Sir Cecil Kisch.

M. Filhol, who is one of our guests from France, is a man who also has great experience in the petroleum world, and he is a man who will be of tremendous benefit to the Committee on which he sits. Sir Ronald Graham is a man of international repute, dealing with men and matters everywhere, and I am sure that he too will be of great benefit to the Committee. Mr. Starling we all know. Unfortunately, he is not able to be with us to-day. He is a man who has put in a tremendous amount of work.

This is the Committee of which I have to propose the toast. Could anyone wish for a nicer job than to propose a toast to these gentlemen, who are so well versed in the subject with which they have to deal, and so well known amongst us? I give you the toast with the very greatest confidence. I am glad to give it. I am glad to think that this Anglo-French Committee has been set up, and I am perfectly certain that it is composed of men who could not be bettered. I give you the toast of "The Permanent Anglo-French Executive Committee for Oil," and I couple with it the names of Colonel Pineau and Sir Cecil Kisch. (*Applause.*)

Replies to Toast.

Colonel L. Pineau, who responded, said: This is the first time that I have had the honour of being your guest as the Chairman of the Anglo-French Executive Committee for Oil, but it is not the first time that I have had the great pleasure of taking luncheon or dinner with you. If this time the circumstances are more serious, and if the honour is greater, the pleasure remains the same.

More than ten years ago I was received as an Honorary Member of the Institution of Petroleum Technologists, which has since acquired titles of nobility and become the Institute of Petroleum. The Institute is the elder brother of the Association Française des Techniciens du Pétrole, whose affectionate greetings I am charged to convey to you, greetings of brothers in arms. (*Applause.*) I am able to tell you that, following your example, the "A.F.T.P." has decided to go on with its work. They will undertake again the editing of their *Bulletin*, and you will have an opportunity of following their work. You will also be able to find in this *Bulletin* news of many French engineers who have taken up arms and are at the front. (*Applause.*)

I have been your host as Chairman of the Permanent Council of World Petroleum Congresses, where I had as colleagues some very good friends like Colonel Auld and Mr. Dewhurst. I have an interesting communication to make to you on the subject of these Congresses. Through a neutral, the Chairman of the Deutsche Mineralölforschung conveyed to me that he is rather concerned about the Third Congress (*laughter*), which, as you know, was to take place in Berlin in June of this year. I was not very surprised. (*Laughter.*) The Germans, I am told, have made every effort to prepare for the Congress, but they desire that the Congress should keep its international character, and their acquaintances have grown fewer; and so they suggest that the Council in its entirety should meet in a neutral country. I wondered whether at the same time we should summon our Austrian, Czech, and Polish friends to the table of the crocodile mentioned by Mr. Winston Churchill! (*Laughter and applause.*)

Finally, I thought it would be better to excuse us for not going, and I answered that certain supplementary work having been thrown on us since September last (*laughter*), we, British and French, were compelled to devote the whole of our time to its execution until it has reached its completion and happy termination by victory. (*Laughter and applause.*)

It is with this aim in view that there has been created the Anglo-French Executive Committee for Oil, in whose name I have the honour of responding to this toast. To tell the truth, the creation of the Executive Committee has only sanctioned a collaboration between the two countries to which we have been accustomed for a very long time. I found again in the Executive Committee as technical adviser your

eminent Past-President and my old friend, Lord Cadman, whose name has been linked with all petroleum policy, whether national or international, for more than twenty years. (*Applause.*) I also found again in the Executive Committee Mr. Starling, with whom for a long time I have had, and still have, the great pleasure of working for Franco-British collaboration on questions of petroleum. Then I have found in the delegation appointed by the British Government newcomers of the first rank—Sir Ronald Graham, who has left on the shores of the Latin Mediterranean the fame of a great ambassador, and, above all, Sir Cecil Kisch, with whom we are on the best possible terms, and who has already become my friend. (*Applause.*)

The Executive Committee for Oil holds its meetings alternately in London and in Paris. This gives to its members the opportunity of making useful comparisons between the situation on the banks of the Thames and the situation on the banks of the Seine; to compare, for instance, the London blackout with the Paris blue-black-out. (*Laughter.*) One is no better than the other, and one gets sprained ankles in both cities! But one notices on both sides of the Channel the same fervour in doing one's duty, the same fierce resolution, the same certainty of victory. I do not believe that history ever recorded an alliance as complete and as close between great peoples engaged in the same cause. (*Applause.*) This cause is the cause of civilization as we have understood it for centuries, we British and French. If we believe Marshal Goering, Germany is to become only a factory, a barrack, a kitchen. Great Britain and France have another ideal! Our ideal is one will, one action, one victory. Let us work for it, and work efficiently, in the way the British so well know when the time comes. Let us follow the precept of the chronicler, at the same time an effective philosopher, when he said "Let us concentrate on action." In war, as in business, action is all that matters. Our principle here is "Let us talk if it is an aid to action, but, if it is an impediment or a substitute, let us keep a purposeful and forceful silence." This principle now invites me to hold my tongue and end my speech. (*Applause.*)

Sir Cecil Kisch, K.C.I.E., C.B., who also responded, said: It is difficult to follow Colonel Pineau, who has voiced so aptly the sentiments that I should like to express myself, but I do most honestly share his view on all the matters to which he has referred. Surely that is a good beginning for an Anglo-French co-operative executive!

I should like to thank Sir Andrew Agnew for the all-too-kindly references that he made to me personally, and to thank him in the name of the Joint Executive for what he said about their task. It is a formidable task that Sir Andrew expounded to you, and I can only say that when I was called into the Ministry of Mines my knees knocked, my octane number was definitely on the low side, and there was an urgent need for lead, but no one was likely to take the responsibility of administering it. I felt—to take the title of a book of which the title is appropriate—as though I was being plunged into Wells of Loneliness. (*Laughter.*) No lead there!

But what do I find around me? I find a host of friends, kindly, sympathetic, and generous, of which this gathering here is an abundant testimony. The Institute of Petroleum, our hosts, have a world-wide reputation. The members are men who have helped to make the industry what it is to-day by their scientific achievements in numerous directions. I understand that the year 1939 was a great year of achievement, but others to follow will be as great, and, I am convinced, greater. An avenue of unlimited promise lies ahead—an avenue "at whose immensity even soaring fancy staggers."

Turning from the general to the concrete, one knows that it is the work done in the science on which this industry depends that is giving our airmen this magnificent aviation spirit which will establish the Allied lead in the air. (*Cheers.*) This is just one illustration of the incalculable value of the Institute's work.

The Oil Executive has been broken in—no, I am using the wrong term; I should say it has been cracked in! (*Laughter.*) I understand—learning slowly, as I am, the special vocabulary of petroleum—that we have been polymerized; that is to say, we have been fused from a large number of units into one single, coherent unit. M. de Monzie, the French Minister for Public Works, who follows our work with the closest interest, observed that the Anglo-French Oil Executive had been fused by "un coup de foudre technique." That is a good start for harmonious work and good results.

The satisfactory functioning of the Executive, the Ministry of Mines, and all who are concerned with petroleum depends on the relations which exist with the great

industry inseparately associated with us in all our tasks. Our relations in time of war have to be characterized by a complete identity of objective and mutual reliance. We are trying to develop these relations in every way, and we had the advantage of the presence yesterday of representatives of the industry at a meeting of the Oil Executive. The Oil Executive and the industry must form one unit in carrying out the great task of which Sir Andrew Agnew spoke. We intend to expand this co-operation, now in full swing under most happy auspices. I may say that in a fairly long experience of public service I have never known such close combination and co-operation as exist to-day between the industry and the Government department which is its representative in the councils of the State. (*Cheers.*)

Petroleum is at the heart of our problems. None of you here will have any difficulty in answering the question, "Daddy, what did you do in the second great war?" You need only say, "I was engulfed in oil." That is at the bottom of everything, and everyone who is in it may fairly feel that he is doing his bit. In this work there are two great tasks before us. The first is to guarantee the large supplies of the products that the French and British require, and the second is the exclusion of those supplies from the enemy. In both those tasks the Direction des Carburants and the Ministry of Mines rely on the co-operation of the great oil industries in France and Britain, and we are receiving that co-operation in ample measure. I should like to add also, following Colonel Pineau, that we work under the guidance of an enthusiastic Minister, who watches our work with close attention.

I do not wish in the present context to mention many names, as my catalogue of friends and colleagues in the work would be too long. Everyone knows, however, that this association with the industry is very close through the work of the Petroleum Board, whose Chairman has just spoken. A long time ago the poet Byron—who was also an expert on oil, though you may not have known or remembered it—wrote:

> "In virtues nothing earthly can surpass her
> Save thine incomparable oil, Macassar!"

Byron was no doubt thinking of the beauty parlour and of the poet's locks; to-day the lines would be a little different, and I suggest that Byron might have written:

> "Unearthly virtues fill thy spirit cool,
> Hail, oil incomparable, tetra-ethyl Pool!"

(*Laughter.*) Sir Andrew Agnew wonders whether I am joking. I am not. I have not licensed my car this quarter, and I offer him the lines to advertise his spirit, free of all royalty or commission!

I must say one word to our Chairman, and, with your permission, I will return the compliment which he paid us by speaking in English and make these remarks in French. (*Continuing in French.*) I wish to take this opportunity to express my lively thanks for the very great skill and knowledge of Colonel Pineau, the Chairman of the Committee. All those who take part in the deliberations of the Committee and who are happy to work under his chairmanship are glad to pay a sincere tribute to the devotion with which he carries out the important tasks which have to be performed during the present critical period.

Sir Andrew has told you something about some of the other members, and I shall not go over the ground again, except to express my regret that Mr. Starling, suffering from the fashionable illness of influenza, is unable to be here, and has asked me to express his regret that he could not be present on this interesting and important occasion. We are glad to have found two admirable bilingual Secretaries—Siamese twins, two hearts that beat as one—who keep the minutes and the members in order with equal facility.

I must now refer to one whose name has already been mentioned, and who has come back to this work—Lord Cadman, who was at the Ministry before, in the last war. Lord Cadman, I am glad to say, has the room next door to mine, so that there is someone who can keep an eye on me—though I do not altogether accept Sir Andrew's imputation! Lord Cadman brings to our work wise counsel, long experience, and understanding of men and matters which are invaluable at a time like this, when so much depends on knowledge and so much depends on the capacity to handle men. I should like to express to him my personal acknowledgements.

All speeches must be rationed in these days, and I think that I have exhausted even my supplementary coupon. (*Laughter.*) But, rationing or no rationing, there

is always one kind of oratory that is satisfactory, and that is finished oratory (*laughter*), and so I should like to conclude by thanking Professor Nash and all you gentlemen who have so generously honoured us on this occasion for your kindness in receiving us, and by saying to our French friends who are here that to-day *Union Sacrée* has a wider meaning, and it is a *Union Sacrés* for us all until we achieve the final goal, victory and peace. (*Applause.*)

The PRESIDENT (Prof. A. W. NASH) said: It is very gratifying to me to-day to see such good support from the members of the Institute at this function. Our greatest pleasure has been to welcome the members of the Anglo-French Executive Committee for Oil and wish them success in their extremely responsible task. Another pleasure in which I feel we all share is that of renewing old friendships and acquaintanceships among our fellow-members; and in that respect particularly we are pleased to welcome our friends Colonel Pineau and M. Filhol, gentlemen whose scientific and technical knowledge we hold in the highest esteem, based as it is on a sound background of petroleum technology and a knowledge of the industrial problems connected therewith, a knowledge which, I should imagine, is most essential in work of the kind on which our French colleagues are now engaged.

This is an opportunity to meet which comes to some of us only on the occasion of the Annual Dinner, and, as you all know, it was deemed advisable to cancel the arrangements for the Annual Dinner, which was to have been held last December. You have also had to forego the usual monthly meetings of the Institute and the advantages of consulting the Institute's library. I feel sure you will allow me to trespass on your time for a few moments, while I give you a little more information than it has been possible to give in printed circulars.

A few days after the war broke out we were compelled by circumstances over which we had no control to vacate our London offices. In the few days we had available, our Secretary lost no time and spared no energy in endeavouring to get other accommodation in London or its outskirts, but without success. Fortunately there was a large room available at the Department of Oil Engineering and Refining at Birmingham University, and I was able to place that room at the disposal of your Council. The Council accepted that offer, and, as you all know, the Institute has been located at Birmingham since last September.

Apart from the fact that the whole of the Institute's business has now to be transacted through the post, the Institute's activities are no more and no less than they would have been if it still retained its offices in London. In the matter of monthly meetings, for example, the Publication Committee had prepared a very interesting and important syllabus of papers for the 1939–40 session, but without exception the authors of those projected papers were transferred to work of great national importance and were compelled to withdraw their promises. On the other hand, the *Journal* has continued publication without intermission, and, so far as I can say at present, will continue to do so. It may be of interest to you to learn that, in spite of many inevitable restrictions and excluding enemy countries, between two and three thousand copies of the *Journal* are posted every month all over the world.

Yesterday your Secretary and I attended a luncheon of the flourishing Northern Branch of the Institute at the Engineers' Club in Manchester, when I addressed our northern members on the subject of aviation fuels and lubricants.

In our period of exile from London, very fortunately we have found many good friends, and to all of them I should now like to tender our most grateful thanks. The Institution of Chemical Engineers have allowed us to use their premises for meetings of the Council and for Committee meetings. The Royal Empire Society have graciously allowed us the use of this very delightful dining-room for the present luncheon. The Institution of Mechanical Engineers and the Imperial College have given us the use of their libraries. The Institute of Fuel have invited our members to their meetings, and finally the Royal Society of Arts have allowed us to hold a meeting this afternoon in their somewhat war-scarred meeting hall—you will understand that statement when you get there—where I hope in a few minutes to have the pleasure of addressing you again. In the meantime, I ask you to show your appreciation of these very real kindnesses and tokens of help with acclamation.

The vote of thanks was carried by acclamation, and the proceedings terminated.